VOL. IV. [MARCH, 1883.] NO. 6.

AMERICAN CHEMICAL JOURNAL.

EXPERIMENTS ON THE GASES OCCLUDED BY COKE.

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No small amount of labor has been expended by chemists in studying the amount and character of the gases held confined by porous solids. Professor Reichardt,[1] of Jena, in particular, and his pupils have published several important papers upon the subject, and many observers have experimented, more or less carefully, upon the gases contained in charcoal, coke, and coal.

With the view of gaining a clearer comprehension of the significance of Reichardt's method of working than was possible from merely reading the memoirs which relate to it, we have performed a number of experiments somewhat similar to his. We have moreover worked in a critical spirit, with the utmost care, and with attention specially directed to a just appreciation of the limitations of such experiments and to the sources of error with which they are beset. The method employed by Reichardt and his disciples was to fill with quicksilver the vessel which contained the substance to be examined, and so expel the air from the vessel, as well as from the interstices between the particles of the substance. The arrangement of the apparatus and the precautions to be observed in

[1] See Reichardt & Blumtritt, Liebig & Kopp's Jahresbericht, 1866, p. 53; Doebrich, *ibid.* 1868, p. 946; Scheermesser, *ibid.* 1871, p. 1059.

using it will be found in Fresenius's Zeitschrift für analytische Chemie, 1868, **7**, 184. The charged flask was heated in a paraffin bath to 140° or 200° as long as gases were evolved, and at the conclusion of the experiment a new portion of mercury was allowed to flow into the flask, in order to push out, through the delivery tube, the last portions of gas which had been expelled from the substance by heating. We have ourselves found a Berlin flask of 75 to 100 cc. capacity well suited for use in this connection and that 20 grams of pulverized coke was a sufficient quantity of material. From this amount of coke we commonly obtained from 15 to 20 cc. of gases.

As will be seen on examining the experiments recorded below, we have repeatedly tested the value of the foregoing method, by comparing the gases obtained by means of it with those got by heating similar samples of coke in a vacuum obtained by means of the Sprengel pump. The results of our trials go to prove that Reichardt's method has merit in so far as it goes; that is to say, a considerable portion of the occluded gases can be expelled by means of it. The results hitherto published by Reichardt and his pupils, as obtained in this way, are undoubtedly valuable; though, as would naturally be expected, the method is less effective than the one based on working in a vacuum. It is manifest, moreover, that even when the Sprengel pump is used, the temperatures of 200°, and less, at which most of our experiments were performed, are not high enough for the complete expulsion of the gases occluded by coke.

Our Sprengel pump was of the form described by S. W. Johnson[1] and E. H. Jenkins. For analyzing the gases obtained from the cokes we employed the apparatus of Doyère as modified by Hinman,[2] which admits of the measurements being made at a constant pressure and temperature. The gases were estimated in the usual way, viz. carbonic acid by absorption with strong potash lye; oxygen by absorption with alkaline pyrogallate of potash, and carbonic oxide by exploding with oxygen admixed with hydrogen and absorbing the resulting carbonic acid with potash lye. Nitrogen was estimated by the difference. It was evident that little if any hydrogen was contained in the gases examined by us. We were never able to explode any sample of the gas with oxygen alone; nor did we notice any appreciable

[1] This Journal, 1880, **2**, 29.

[2] American Journal of Science, 1874, **8**, 182.

contraction of the original volume on exploding after addition of a mixture of oxygen and hydrogen. This apparent absence of hydrogen is a point which needs to be carefully studied. We have postponed the consideration of it, since it seemed to have no immediate bearing on the comparisons we were actually making.

When no mention is made of other gases than carbonic acid and oxygen in the following description of details, it is to be understood that the analysis was carried no further, and that no effort was made to determine carbonic oxide or hydrogen in those special cases. On the other hand, in every instance where the amount of nitrogen is recorded, the presence or absence of carbonic oxide was proved.

All the cokes examined by us were from the Boston Gas Light Company. They were well burnt, as the term is, *i. e.* thoroughly deprived of illuminating gas. The custom at the works is to keep each charge of coal in its retort during four hours at a temperature not far from 2000° F.[1] The retorts are of clay 9′×15″×26″, and they are worked in connection with exhausters which reduce the pressure within them to the value of a column of water a quarter inch in height.

Series I.—*Air-Dried Coke from a Dwelling-house.*

We first examined some coke which had lain nearly a year in the dry cellar of a dwelling-house. A powdered portion of it gave off 2.7 per cent. of moisture when heated for an hour and a half at 110° in an air-bath. It may here be said that in most instances the cokes examined by us were powdered finely enough to pass through a sieve the orifices of which were one millimetre in diameter. In three instances, however, viz. in Exps. B, C, and Z, the holes of the sieve were two millimetres wide. Twenty grams of the finer coke compacted rather firmly in a measuring cylinder occupied a space of 30 cubic centimetres.

Three separate portions of the coke were heated at different times according to Reichardt's method in a paraffin bath, with the following results:

A. 22 grams of the coke were taken. On heating for half an hour at 80° C. no gas was obtained. During the next half-hour at

[1] According to determinations made by me, on the assumption that the specific heat of wrought iron is 0.126 at this temperature.—D. S. Lewis.

100° rather more than 4 cc. of gas came off; during the next 15 minutes at 120° about 5 cc. were obtained, and during the next hour, at 150°, 6 or 7 cc. In the gas obtained up to 150° there was found 31.09 per cent. of carbonic acid and 25.39 per cent. of oxygen, some of which came, of course, from air that was loosely entangled by the coke and had not been completely expelled when the flask was filled with the mercury. The same coke was heated further for half an hour at 180°, when 4 cc. more of gas came off, and for an hour and twenty minutes at 200°, when 4 cc. or so of gas were obtained. This gas obtained between 150° and 200° was found to contain 65.60 per cent. of carbonic acid, but the amount of oxygen in it was too small to measure.

In brief, the 22 grams of coke (A) heated to 200° gave in all 22½ cc. of gas (accurately measured[1]), which contained 43.03 per cent. of carbonic acid and a very considerable amount of oxygen, as well as nitrogen.

B. 13 grams of the coke somewhat coarser than the preceding sample, heated 30 minutes at 100°, gave about 6 cc. of gas; 15 minutes at 120° about 4 cc.; one hour at 150° about 4 cc.; and one hour at 200° 2 cc. Accurately measured, 13 grams of the coke heated to 200° gave 15 cc. of gas which contained 41.43 per cent. of carbonic acid, 5.74 per cent. of oxygen, and 52.83 per cent. of nitrogen.

C. 19 grams of the coke similar to B, heated 15 minutes to 100°, gave about 8 cc. of gas, for one hour at 150° 8 cc. and for one hour at 200° rather more than 5 cc., or all told, 19 grams of coke heated to 200° gave 22 cc. of gas which contained 42.50 per cent. of carbonic acid, 6.49 per cent. of oxygen, and 51.01 per cent. of nitrogen.

The five following samples (D to H) of the same air-dried coke were heated in a paraffin bath, as before, but the flask which contained the coke was now connected with a Sprengel pump, by means of which the air originally contained in the flask and that entangled by the particles of coke was removed in the first place before the flask was heated. A vacuum was of course maintained throughout the experiment, *i. e.* the pump was kept in action to facilitate the escape of the gases from the coke and to remove them from the flask immediately.

[1] It is to be understood that in many instances the amounts of gas obtained at the intermediate temperatures were estimated roughly, *i. e.* without any attempt at accurate measurement. The final measurements, and all those upon which the analyses depended, were of course made with the most scrupulous care.

D. 21 grams of the coke were taken. The air exhausted from the flask before heating was found to contain 0.19 per cent. of carbonic acid and 19.77 per cent. of oxygen.[1] On heating the coke to 75° only a small quantity of gas came off. On heating half an hour at 100° about 5 cc. of gas were obtained; for 45 minutes at 150° 3 cc., and for one hour at 200° 6 or 8 cc. more. In all, the 21 grams coke heated to 200° in connection with the Sprengel pump gave 17 cc. of gas, which contained 62.97 per cent. of carbonic acid, 5.31 per cent. of oxygen, and 31.72 per cent. of nitrogen.

E. 40 grams of the coke were taken, and the apparatus was exhausted of air at the ordinary temperature. On subsequently heating one hour at 100° 12½ cc. of gas were collected; which, on analysis, was found to contain 41.97 per cent. of carbonic acid, 11.72 per cent. of oxygen, 1.45 per cent. of carbonic oxide, and 44.86 per cent. of nitrogen. On heating one hour longer at 200° 17½ cc. more of gas came forward which contained 57.48 per cent. of carbonic acid, 3.25 per cent. of oxygen, 4.97 per cent. of carbonic oxide, and 34.30 per cent. of nitrogen. The total 30 cc. of gas obtained by heating the 40 grams of coke to 200° contained 51.03 per cent. of carbonic acid, 6.77 per cent. of oxygen, 3.50 per cent. of carbonic oxide, and 38.70 per cent. nitrogen.

F. 41 grams of the coke were placed in the flask, and in order to try whether the material could be completely freed from entangled air, there was carried to the bottom of the coke a tube through which purified nitrogen gas was forced during half an hour, at the ordinary temperature and pressure of the air. This nitrogen was proved by analysis to contain neither oxygen nor carbonic acid before it was admitted to the flask. On testing, at the close of the half-hour, the gas which had come forward, it was found to contain 5.28 per cent. of oxygen, but no carbonic acid. The pure nitrogen was passed through the coke during a second half-hour, and was then found to be free from both oxygen and carbonic acid. The apparatus was now left to stand for a day and a half full of the pure nitrogen, and at the end of this time a current of the nitrogen was passed through the coke during twenty minutes, but on testing the outcoming nitrogen neither oxygen nor carbonic acid was detected, at least not in measurable quantities. After the nitrogen had been pumped out of the flask the latter was heated

[1] In another experiment, the air exhausted from a flask containing 24 grams of this kind of coke was found to contain 0.4 per cent. carbonic acid, 20.77 per cent. oxygen, and 78.83 per cent. nitrogen.

for an hour at 100° ; 10¼ cc. of gas came forward, which contained 35.26 per cent. carbonic acid, 5.40 per cent. oxygen, 2.84 per cent. carbonic oxide, and 56.50 per cent. nitrogen. On heating during another hour at 200° 16½ cc. of gas came off, the composition of which was 79.93 per cent. carbonic acid, 0.3 per cent. oxygen, 4.22 per cent. carbonic oxide, and 15.55 per cent. nitrogen. In all, the 41 grams coke yielded 27 cc. of gas when heated up to 200°, and the gas contained 62.57 per cent. of carbonic acid, 2.29 per cent. oxygen, 3.69 per cent. carbonic oxide, and 31.45 per cent. nitrogen.

G. 20 grams of the coke were treated with the purified nitrogen, as in F, during two half-hour terms, and the outcoming gas was proved to be free from oxygen and carbonic acid. The Sprengel pump was then set in action for 15 minutes, and the gas thus obtained was tested. A trace of oxygen, but no carbonic acid, was found in it. The coke was then heated for an hour at 100° and 11 cc. of gas were obtained, which contained 25.53 per cent. carbonic acid, 6.27 per cent. oxygen, 0.46 per cent. carbonic oxide, and 67.74 per cent. nitrogen. On heating during another hour at 200° 16¼ cc. of gas were obtained, which contained 68.78 per cent. carbonic acid, 2.54 per cent. oxygen, 0.68 per cent. carbonic oxide, and 28.00 per cent. nitrogen. In all, the 20 grams coke heated to 200° gave 27¼ cc. gas, which contained 51.46 per cent. carbonic acid, 4.06 per cent. oxygen, 0.59 per cent. carbonic oxide, and 43.89 per cent. nitrogen.

H. 18 grams of the coke were treated with nitrogen, as in G, for half an hour at the ordinary pressure of the air, at the end of which time neither oxygen nor carbonic acid was found in the outcoming gas. The pump was then put in action, and traces of both oxygen and carbonic acid were detected in the gas thus obtained. The apparatus full of nitrogen was left at rest for a day and a half and then exhausted at the ordinary temperature. The 79 cc. of gas examined contained 0.59 per cent. carbonic acid and 5.53 per cent. oxygen. The pump being kept in action, the coke was heated one hour to 100° and 5¼ cc. of gas were obtained, which contained 33.08 per cent. of carbonic acid, 6.15 per cent. oxygen, 0.96 per cent. carbonic oxide, and 59.81 per cent. nitrogen. On heating during another hour to 200° 10 cc. of gas were obtained, which contained 76.25 per cent. carbonic acid and 0.5 per cent. oxygen. The other constituents were not determined. In all, the 18 grams coke heated to 200° gave 15¼ cc. of gas which contained

61.50 per cent. carbonic acid and 2.43 per cent. oxygen, as well as some carbonic oxide and nitrogen.

SERIES II.—*Air-Dried Coke from Store-house.*

This coke had been lying two years in a dry store-house at the gas works in Boston.

I. 24 grams of the coke heated in Reichardt's manner during 15 minutes at 100° gave some 10 cc. of gas; for 30 minutes at 150°, 10 cc., and for one hour at 200°, 9 cc. In all, 29 cc. of gas, which contained 32.75 per cent. carbonic acid, 8.21 per cent. oxygen, and 59.04 per cent. nitrogen.

J. 25 grams of the coke were put in a flask and the air was exhausted, at the ordinary temperature, with the Sprengel pump. It was found to contain 0.09 per cent. carbonic acid and 20.15 per cent. oxygen. On heating the coke for half an hour at 100°, about 4 cc. of gas were obtained; for 45 minutes at 150°, 3 or 4 cc., and for an hour and a half at 200°, 5 or 6 cc. In all, 14¾ cc. which contained 61.37 per cent. carbonic acid, 4.82 per cent. oxygen, and 33.81 per cent. nitrogen.

K. 44 grams of the coke were put in a flask into which some recently boiled and cooled water was poured, and the apparatus was connected with the Sprengel pump and exhausted. On heating an hour and a half at 100°, some 4 cc. of gas were obtained, which contained 11.46 per cent. carbonic acid, 3.66 per cent. oxygen, and 84.88 per cent. nitrogen. On heating an hour at 200°, 20⅓ cc. of gas were obtained, which contained 76.32 per cent. carbonic acid and 0.44 per cent. oxygen. In all, the 44 grams coke heated to 200° gave 24⅓ cc. gas, which contained 65.42 per cent. carbonic acid and 0.98 per cent. oxygen, besides nitrogen.

L. 21 grams of the coke were placed in a flask, and nitrogen gas of assured purity was passed through it during 45 minutes; the pump was also filled with the nitrogen, and the whole apparatus was left at rest for four days at the pressure of the air. Under these conditions it appeared that a little carbonic acid and oxygen diffused out from the coke into the nitrogen gas, for on exhausting the apparatus and analyzing the 67½ cc. of "nitrogen" obtained, it was found to contain 1.11 per cent. carbonic acid and 1.88 per cent. oxygen. On subsequently heating the coke for one hour at 100°, and another hour at 200°, 17¼ cc. of gas were obtained, which contained 64.68 per cent. carbonic acid and 0.41 per cent. oxygen.

M. 41 grams of the coke were put in a flask and a current of

pure nitrogen gas was passed through it for 45 minutes at the ordinary temperature and pressure. The outcoming gas was found to be free from carbonic acid and oxygen. The Sprengel pump was then connected with the flask and filled with the nitrogen, and the apparatus was left at rest during four days at a pressure slightly less than that of the atmosphere. On then exhausting the flask 26 cc. of the "nitrogen" were collected for examination. It contained 1.28 per cent. carbonic acid and 2.40 per cent. oxygen. On heating the coke to 100° for an hour, 6 cc. of gas were obtained, which contained 56.26 per cent. carbonic acid, 1.2 per cent. oxygen, and 42.54 per cent. nitrogen. On heating during another hour at 200°, 21 cc. of gas were obtained, which contained 79.66 per cent. carbonic acid, 0.19 per cent. oxygen, 1.55 per cent. carbonic oxide, and 18.60 per cent. nitrogen. In all, the 41 grams of coke heated to 200° gave 27 cc. of gas, which contained 74.51 per cent. carbonic acid, 0.42 per cent. oxygen, 1.21 per cent. carbonic oxide, and 23.86 per cent. nitrogen.

SERIES III.—*Old Coke, from out-of-doors.*

This coke had been left in a heap exposed to the weather for three years or more in a storage yard a mile or two from the gas works.

N. 22 grams of the coke heated, in Reichardt's manner, one hour at 200° gave 22 cc. of gas, which contained 28.31 per cent. carbonic acid, 9.02 per cent. oxygen, and 62.67 per cent. nitrogen.

O. 23 grams of the coke were taken, air was exhausted from the flask with the Sprengel pump, and the coke was then heated one hour at 200°; 9½ cc. of gas were obtained, which contained 54.66 per cent. carbonic acid and 4.29 per cent. oxygen, besides nitrogen.

P. 23 grams of the coke having been placed in a flask, recently boiled and cooled water was added and the air exhausted at the ordinary temperature. On then heating the coke one hour at 100° 3 cc. of gas were obtained, which contained 6.65 per cent. carbonic acid and 6.01 per cent. oxygen, besides nitrogen. On heating for another hour at 200° 6½ cc. of gas came forward, which contained 74.27 per cent. carbonic acid and 0.31 per cent. oxygen, besides nitrogen. In all, 23 grams of coke gave 9½ cc. of gas containing 52.22 per cent. carbonic acid and 2.17 per cent. oxygen.

Q. 45 grams of coke were put in a flask, cooled boiled water was added and the apparatus was exhausted at the ordinary tem-

perature. On then heating the coke one hour at 100° 5¾ cc. of gas were obtained, which contained, besides nitrogen, 17.31 per cent. carbonic acid and 1.05 per cent. oxygen. On heating during another hour at 200° 12 cc. of gas were obtained, which contained 67.57 per cent. carbonic acid and 2.70 per cent. oxygen. In all, the 45 grams coke gave 17¾ cc. of gas containing 51.22 per cent. carbonic acid and 2.16 per cent. oxygen.

In another trial, water was boiled directly in the flask, and after it had cooled, 22 grams of coke were added, the Sprengel pump was connected and the apparatus exhausted. On heating the coke for half an hour to 80° 1 cc. of gas came off, for an hour and twenty minutes longer at 80° half a cc., for half an hour at 100° half a cc., for half an hour up to 200° 2 cc., and for another half-hour at 200° half a cc.; accurately measured, the 22 grams of coke heated to 200° gave 5¾ cc. gas which contained 18.06 per cent. carbonic acid, 1.49 per cent. oxygen, and 80.45 per cent. nitrogen. We are unable to account for the lack of accordance between these results and those obtained in experiments P and Q.

R. 39 grams of the coke were put in a flask, the apparatus was exhausted and left to stand two days and a half at the ordinary temperature. On then pumping anew, without any application of heat, 4 cc. of gas were obtained which contained 8.65 per cent. carbonic acid, 12.74 per cent. oxygen, and 78.61 per cent. nitrogen. On now heating to 100° for one hour 5½ cc. gas were obtained, which contained 57.64 per cent. carbonic acid, 3.13 per cent. oxygen, and 39.23 per cent. nitrogen. On heating to 200° during another hour 7¾ cc. of gas were obtained, which contained 75.96 per cent. carbonic acid, no oxygen (!), 0.68 per cent. carbonic oxide, and 23.36 per cent. nitrogen. In all, the 39 grams of coke heated to 200° gave nearly 17 cc. of gas which contained 53.52 per cent. carbonic acid, 4.14 per cent. oxygen, 0.39 per cent. carbonic oxide, and 41.95 per cent. nitrogen.

S. 42 grams of the coke were put in a flask, and pure nitrogen gas was passed through it for half an hour at the ordinary temperature and pressure, when a sample of the outcoming gas was collected for analysis. It contained no oxygen, but 2.35 per cent. of carbonic acid. Nitrogen was passed through the coke during another half-hour, and a sample then taken was found to contain no oxygen, as before, and 1.41 per cent. carbonic acid. The nitrogen was passed through the coke yet another half-hour, when the flask was put in connection with the pump and exhausted of

its gaseous contents. On then heating the coke to 100° for one hour 10 cc. of gas were obtained, which contained 47.18 per cent. carbonic acid and 1.11 per cent. oxygen. On heating to 200° during another hour 13¾ cc. of gas were collected, which contained 70.63 per cent. carbonic acid and a third of a per cent. of oxygen. In all, the 42 grams of coke heated to 200° gave 23¾ cc. of gas, which contained 60.78 per cent. carbonic acid and 1.10 per cent. oxygen, besides nitrogen. It appeared in this case that by using nitrogen gas to clear out the flask the oxygen entangled by the coke was removed more completely than could be done in the case of the thoroughly air-dried coke of Exps. F, G, and H. We are ignorant as to whether this fact is in any way connected with the presence of the larger proportion of moisture which was contained in the coke which had lain out-of-doors, but that this old coke differed decidedly in some way from the other cokes examined by us is shown by the circumstance that it gave up a smaller proportion of carbonic acid than any of the other cokes, excepting the one taken directly from a gas retort. It will be of interest to determine whether, generally speaking, other specimens of old, weathered coke contain a correspondingly small proportion of carbonic acid, for the fact might possibly have some influence on the kindling temperature of the material. A somewhat similar remark is suggested by the small amount of carbonic acid obtained in Experiments Y, Z, and AA (beyond), from coke taken directly from a gas retort and cooled without wetting. It has been noticed in Boston that many people who habitually use coke as fuel prefer that which has lain in the storage yards, though the reason of this preference may be that some sulphur has been eliminated from the coke by the weathering, and perhaps that the coke is less thoroughly saturated with water than that delivered directly from the gas works immediately after it has been quenched. It would be hard to judge, without further investigation, as to the bearings upon this question of De Saussure's[1] observations that charcoal absorbs much less carbonic acid when wet than when dry, and that dry charcoal charged with carbonic acid gives up a considerable part of the gas when wetted.

Series IV.—*Recent, partially-dried Coke.*

This coke had been made about a fortnight before our examination of it. After having been quenched with water in the usual

[1] Gilbert's Annalen der Physik, 1814, **47**, 120.

way, it had been carried to a storage yard and left there under a roof, *i. e.* in a shed open at the sides.

T. 21 grams of the coke heated in Reichardt's manner during fifteen minutes at 100° gave some 12 cc. of gas, heated thirty minutes at 150° it gave 6 cc., and for an hour at 200° about 4 cc. In all, the 21 grams of coke heated to 200° gave 22⅜ cc. gas, and the gas contained 32.45 per cent. carbonic acid, 1.81 per cent. oxygen, 4 per cent. carbonic oxide, and 61.74 per cent. nitrogen.

U. 21 grams of the coke were put in a flask, which was then exhausted with the Sprengel pump at the ordinary temperature. On heating the coke up to 150° 3 cc. of gas were collected, and on heating half an hour at 200° 6 cc. came forward. In all, the 21 grams coke gave 9 cc. of gas, which contained 72.45 per cent. carbonic acid and 2.33 per cent. oxygen.

V. 22 grams of the coke treated similarly to that of the foregoing experiment (U), but heated immediately to 200° and maintained at that temperature during three hours, gave 12¾ cc. of gas, which contained 73.01 per cent. carbonic acid, 1.57 per cent. oxygen, and 25.42 per cent. nitrogen.

W. 39 grams of the coke were allowed to stand at the ordinary temperature during four days in a flask from which the air had been exhausted. On again exhausting the flask 3½ cc. of gas were obtained, which contained 5.95 per cent. carbonic acid, 5.38 per cent. oxygen, and 88.67 per cent. nitrogen. On then proceeding to heat the flask to 100° for an hour, 6¼ cc. of gas were obtained, which contained 97.93 per cent. carbonic acid, and so little of other ingredients, besides nitrogen, that the amounts of them could not be measured. On heating to 200° for an hour 14¾ cc. of gas were obtained, which contained 82.58 per cent. carbonic acid, 1.49 per cent. oxygen, 2.23 per cent. carbonic oxide, and 13.70 per cent. nitrogen. In all, there were obtained from the 39 grams coke up to 200° 24½ cc. gas which contained 75.5 per cent. of carbonic acid. The 21 cc. gas obtained by actually heating, first to 100° and then to 200°, contained 87.16 per cent. carbonic acid.

X. 26 grams coke were kept in an exhausted tube of hard glass for 2½ days at the ordinary temperature of the air; nearly 5½ cc. of gas were obtained, which contained 8.29 per cent. carbonic acid, 16.02 oxygen, and 75.69 per cent. nitrogen. On then heating the tube to low redness for 20 minutes some 35 cc. of gas were obtained, which was evidently nearly all that could be expelled from the coke at that temperature. On analysis, the gas was found to con-

tain 78.47 per cent. carbonic acid and 0.55 per cent. oxygen. An accident prevented the determination of the other constituents of the sample. On heating the tube 20 minutes longer, to intense redness, 40 cc. more of gas came forward, and still more might have been obtained had not the tube cracked. The gases obtained at the ordinary temperature and at low redness, taken together, contained 62.37 per cent. carbonic acid and 4.10 per cent. oxygen. There were 40½ cc. of this gas, let alone the 40 cc. obtained at the higher temperature.

SERIES V.—*Coke taken immediately from a Gas Retort.*

The coal from which this coke was obtained had been heated in one of the ordinary gas retorts at the works during four hours in the usual way. The coke drawn from the retort in a state of ignition was not wetted, but was cooled in closed vessels expressly for our experiments.

Y. 24 grams of the coke heated, in Reichardt's manner, for 15 minutes at 100° gave some 10 cc. of gas, for 30 minutes at 150° about 10 or 12 cc. more, and for one hour at 200° about 10 cc. more. In all, the 24 grams coke heated to 200° gave 33 cc. gas, which contained 7.36 per cent. carbonic acid, 5.10 per cent. oxygen, and 87.54 per cent. nitrogen.

Z. 14 grams of the coke heated, in Reichardt's manner, for 15 minutes at 100° gave 5 cc. of gas, for 30 minutes at 150° 6 or 7 cc., and for one hour at 200° 5 or 6 cc. In all, the 14 grams of coke heated to 200° gave 17½ cc. of gas, which contained 15.64 per cent. carbonic acid, 7.71 per cent. oxygen, and 76.65 per cent. nitrogen.

AA. 24 grams of the coke, heated in Reichardt's manner, 15 minutes at 100° gave some 10 cc. of gas, 15 minutes at 150° 8 or 9 cc., and 45 minutes at 200° 12 or 13 cc. In all, the 34 grams of coke heated to 200° gave 33 cc. of gas, which contained 7.71 per cent. carbonic acid and 9.23 per cent. oxygen.

BB. This experiment was tried with some of the coke that was taken directly from a gas retort, but which, after having been powdered, had been left in a corked bottle for two months before it was subjected to examination. It will be noticed that the Sprengel pump was used in this instance, but not in the experiments Y, Z, and AA. 41 grams of the coke were taken. The flask was exhausted before heating it, and then kept at 100° for one hour. 16½ cc. of gas were obtained, which contained 11.86 per cent. carbonic acid, 15.47

per cent. oxygen, 1.10 per cent. carbonic oxide, and 71.57 per cent. nitrogen. On heating for another hour at 200° 19½ cc. of gas were obtained, and this gas contained 29.42 per cent. carbonic acid, 0.36 per cent. oxygen, 1.9 per cent. carbonic oxide, and 68.22 per cent. nitrogen. In all, the 41 grams of coke heated to 200° gave 36 cc. of gas, which contained 21.39 per cent. carbonic acid, 7.27 per cent. oxygen, 1.53 per cent. carbonic oxide, and 69.81 per cent. nitrogen.

For the sake of ready comparison, those results of the two methods of working—viz. with and without the use of the Sprengel pump—which are directly comparable are here given in tabular form:

	Heated to 200° C. At ordinary pressure of air.			Heated to 200° C. In Vacuo.				
SERIES I.—*Air-dried Coke from Dwelling-house.* Per cent. of:	A.	B.	C.	D.	E.	F.	G.	H.
Carbonic Acid	43.03	41.43	42.50	62.97	51.03	62.57	51.46	61.50
Oxygen	...	5.74	6.49	5.31	6.77	2.29	4.06	2.43
Carbonic Oxide	...	...	...	...	3.50	3.69	0.59	...
Nitrogen (by difference)	...	52.83	51.01	31.72	38.70	31.45	43.89	...
		100.00	100.00	100.00	100.00	100.00	100.00	
SERIES II.—*Air-dried Coke from Store-house.*		I.		J.	K.		L.	M.
Carbonic Acid		32.75		61.37	65.42		64.68	74.51
Oxygen		8.21		4.82	0.98		0.41	0.42
Carbonic Oxide		...		...	...		...	1.21
Nitrogen (by difference)		59.04		33.81	...		...	23.86
		100.00		100.00				100.00
SERIES III.—*Old Coke from Out-of-doors.*		N.		O.	P.	Q.	R.	S.
Carbonic Acid		28.31		54.66	52.22	51.22	53.52	60.78
Oxygen		9.02		4.29	2.17	2.16	4.14	1.10
Carbonic Oxide		...		...	...	...	0.39	...
Nitrogen (by difference)		62.67		...	...	...	41.95	...
		100.00					100.00	
SERIES IV.—*Recent, partially-dried Coke.*		T.		U.		V.		W.
Carbonic Acid		32.45		72.45		73.01		75.50
Oxygen		1.81		2.33		1.57		...
Carbonic Oxide		4.00		...		...		...
Nitrogen (by difference)		61.74		...		25.42		...
		100.00				100.00		
SERIES V.—*Coke from the Gas-retort.*	Y.	Z.	AA.			BB. (After standing for two months in a bottle.)		
Carbonic Acid	7.36	15.64	7.71			21.39		
Oxygen	5.10	7.71	9.23			7.27		
Carbonic Oxide	...	...	...			1.53		
Nitrogen (by difference)	87.54	76.65	...			69.81		
	100.00	100.00				100.00		

On examining the foregoing results it will be seen that the gas expelled from the cokes at 100° almost invariably contained a smaller percentage of carbonic acid and a larger proportion of oxygen than were found in the gas obtained by heating to 200°. Compare experiments E, F, G, H, K, M, P, R, S, BB; and the exceptions Q (less oxygen), and W (more carbonic acid). Manifestly the larger amounts of oxygen, and of nitrogen also, that are obtained at the lower temperature must keep down the proportion of carbonic acid in the measuring tube. So too we have always found a comparatively large proportion of nitrogen in those samples of gas which were obtained by working in Reichardt's manner; a fact which is in full accord with our inability to drive off, in this way, from the coke as much of the occluded carbonic acid as was readily removed by means of the Sprengel pump. For the nitrogen obtained by operating by Reichardt's method being less diluted with carbonic acid than that got with the Sprengel pump, must necessarily seem to be predominant. It is not impossible that the large amounts of nitrogen found in so many different solids by Reichardt and Blumtritt[1] in their experiments might have been appreciably lessened if a better chance had been offered for occluded carbonic acid to escape. In any event the experiments of Reichardt and Blumtritt go to show that a part at least of the nitrogen occluded by solids escapes rather easily on heating. The same thing is to be inferred from the observation of Angus Smith,[2] who found that "nitrogen and hydrogen, when absorbed by charcoal, diffuse into the atmosphere of another gas with such force as to depress the mercury three-quarters of an inch." De Saussure[3] found long ago that much of the nitrogen and hydrogen absorbed by dry charcoal is readily discharged again when the coal is immersed in water.

It seems plain at all events that the carbonic acid obtained by either of the methods employed by us must have really been held as such in the cokes at the beginning of the experiments, and that it was not formed during the experiments by the action of entangled oxygen upon the heated carbon, as might perhaps have been inferred from the observations of Angus Smith[4] on the action of oxygen on charcoal, and possibly from those of Varrentrap[5] re-

[1] Journal für praktische Chemie, 1866, **98**, 426 to 479.
[2] Proceedings of Royal Society, 1863, **12**, 425.
[3] Gilbert's Annalen der Physik, 1814, **47**, 122. [4] *Loc. cit.*
[5] Dingler's Polytechnisches Journal, 1865, **175**, 156, and **178**, 379.

lating to the oxidation of organic matters at temperatures higher than 100°.

It may here be said that we have seen nothing in the course of our investigations to indicate that there was any appreciable action of oxygen upon the coke at temperatures no higher than 200° during the time actually devoted to an experiment. Reichardt[1] also, for his part, was convinced that no such oxidation need be feared; for he directs that "in cases where the temperature is to be no higher than 200°, a bit of linen may be employed, without harm, instead of a disk of wire-gauze, to hold the powdered substance in the flask." But on the other hand the increase of carbonic acid in that portion of our "coke taken directly from a retort" (Series IV, BB), which had been kept in a bottle during two months, goes to show that slow oxidation of the coke by means of oxygen absorbed from the air may perhaps have occurred in that particular case.[2]

It is noticeable that the amounts of oxygen obtained from the coke are usually sufficient, and in some instances more than sufficient, to account for all of this gas which could possibly have been present in the flask at the beginning of the experiment in the form of entangled air.

A large proportion of the nitrogen recorded in our analyses was doubtless actually expelled from the cokes on heating them. No great amount of it can be justly accredited to the entangled air.

In general, we were unable, either by means of nitrogen or boiled water, or by pumping at the ordinary temperature, to get rid of all the atmospheric air which clung to the coke, though in several instances we reduced the proportion of it very decidedly. It appeared that the gas which came forward on using the pump without heating the coke was practically atmospheric air (compare exps. D and J). On allowing samples of coke to remain in a vacuum from 2 to 4 days, at the ordinary temperature of the air, small quantities of gas were given off which contained more oxygen and less carbonic acid than the gas obtained by heating. In one

[1] Fresenius's Zeitschrift, 1868, **7**, 186.

[2] For several successive years, in heaps containing a ton or two of coke which had been thoroughly wetted in the process of quenching and then left to dry slowly under cover, I have noticed that after two or three months there are formed, upon some fragments of the coke, mammillated incrustations, often of considerable superficial extent, of crystallized calcite. Both the appearance of these incrustations and the circumstances under which they were formed seemed to show that the carbonic acid as well as the lime had been derived from the coke itself.—F. H. Storer.

case the gas obtained in the cold in this way amounted to $\frac{1}{10}$, and in another instance to $\frac{1}{3}$ of the volume subsequently obtained by heating the coke to 200° (compare exps. R and W and X). As a rule, however, it was not until the coke was heated that the last portions of the entangled air passed over into the collecting tube, together with gases actually expelled from the coke. It was in order to do away with this difficulty if possible, and in any event to test the significance of it, that we made the attempts to completely expel the entangled air either by immersing the coke in boiled water, or by subjecting it to a current of pure nitrogen gas, as has been recorded above. Some air was undoubtedly expelled by both these devices, though the influence of the operation on the final results of the experiment was not very great (see for example experiments O, P, Q and R). When water was used to expel the air, more or less trouble was occasioned by its condensing in the Sprengel-pump and in the tubes used for collecting the gas. The pure nitrogen gas served a better purpose than the boiled water, but it still appeared that the air entangled by the coke did not diffuse into this cleansing nitrogen so readily as might have been wished. It should be said that we made no special effort to drive out the last traces of gas from the cokes by long-continued heating at any one particular temperature. It seldom happened, for example, that the temperature of 200° was maintained until gas absolutely ceased to come forward, and we have little doubt that in some instances small additional quantities of gas might have been obtained by longer-continued heating at that temperature. So too in the experiments where tubes containing coke were heated to redness, in connection with the Sprengel-pump, rather more gas could have been got if the tubes had been heated longer at that particular temperature. We intended to push these trials further, and to maintain the highly-heated tubes at special temperatures during definite times similar to those adopted in the foregoing experiments. Such experiments would have been specially interesting in enabling us to compare our work more nearly with that of Parry[1] than we have thus far been able to do. We hope to accomplish this purpose at some future day.

Examination of Coke Cinders.—A number of half-burned pieces of coke were picked out from the ashes of a fire which had recently burnt out upon a grate; they were ground to powder and

[1] Chemical News, **25**, 98; and, further, American Chemist, **4**, 254.

tested in connection with the Sprengel pump. One portion of the material weighing 28 grams was put in a flask, and, after the air had been exhausted, it was heated during one hour at 100° and during another hour at 200°. Five cc. of gas were obtained in all, which contained 4.32 per cent. of carbonic acid and 11.11 per cent. of oxygen. Another portion of the cinders weighing 42 grams, similarly treated, gave 7 cc. of gas, which contained 25.64 per cent. of carbonic acid, 9.96 per cent. of oxygen, and 64.40 per cent. of nitrogen.

Examination of Calcined Loam.—Loam from an old pasture was roasted in a muffle, at the lowest possible temperature, until the organic matter was completely destroyed, and the product was subjected to experiment. 27 grams of the calcined earth were placed in a flask, the air was exhausted, and a 14 cc. sample of the outcoming air was collected for analysis. It was found to contain 0.36 per cent. of carbonic acid and 19.67 per cent. of oxygen. The earth was then heated for one hour at 100° and for another hour at 200°, but the amount of gas obtained was too small to measure; yet when another 25-gram portion of the earth was heated during two hours at 200°, after the air had first been pumped out of the flask, it gave 12 cc. of gas which contained 5.84 per cent. of carbonic acid, 15.43 per cent. of oxygen, and 78.73 per cent. of nitrogen. Curiously enough, another 67-gram portion of the earth behaved like the first. After the air had been exhausted from the flask the latter was heated one hour at 200°, then allowed to stand a day and a half, and again heated during three hours at 200°. But the amount of gas obtained was too small to measure and analyze. On the other hand, a measurable quantity of gas was obtained from a 31-gram portion of the earth heated two hours at 200°, but this gas was accidentally lost. As was the case with the coke cinders mentioned above, we think it probable that these differing results may depend upon a lack of homogeneity in the material operated upon. In yet another trial 90 grams of the calcined loam were placed in a flask, the air was exhausted, and the apparatus allowed to stand with the earth *in vacuo* for four days. On then heating two hours at 200°, 6 cc. of gas were obtained which contained 25.84 per cent. of carbonic acid, 10.76 per cent. of oxygen and 63.40 per cent. of nitrogen. The results of this trial are manifestly more trustworthy than those of the preceding tests. It may be remarked in this connection that we had already, sev-

eral years ago, proved qualitatively the presence of carbonic acid in calcined loam such as this now under consideration (see Bulletin of the Bussey Institution, **2**, 204). Finally, another 28-gram portion of the calcined loam was placed in a tube of hard glass, the air was exhausted, and the tube heated to low redness for an hour; 7 cc. of gas were obtained which contained 72.74 per cent. of carbonic acid and 6.46 per cent. of oxygen. The proportion of oxygen is noticeably large in all three of the experiments upon calcined earth; and so it was in the case of the coke-cinders also. The latter were of course admixed with more or less ashes that adhered to them. We have to thank our assistant, Mr. D. T. Hinckley, B. A. S., for efficient aid in this investigation.

Laboratory of the Boston Gas Light Co.

DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.[1]

Second Paper.

By Prof. J. W. Mallet, F. R. S.
University of Virginia.

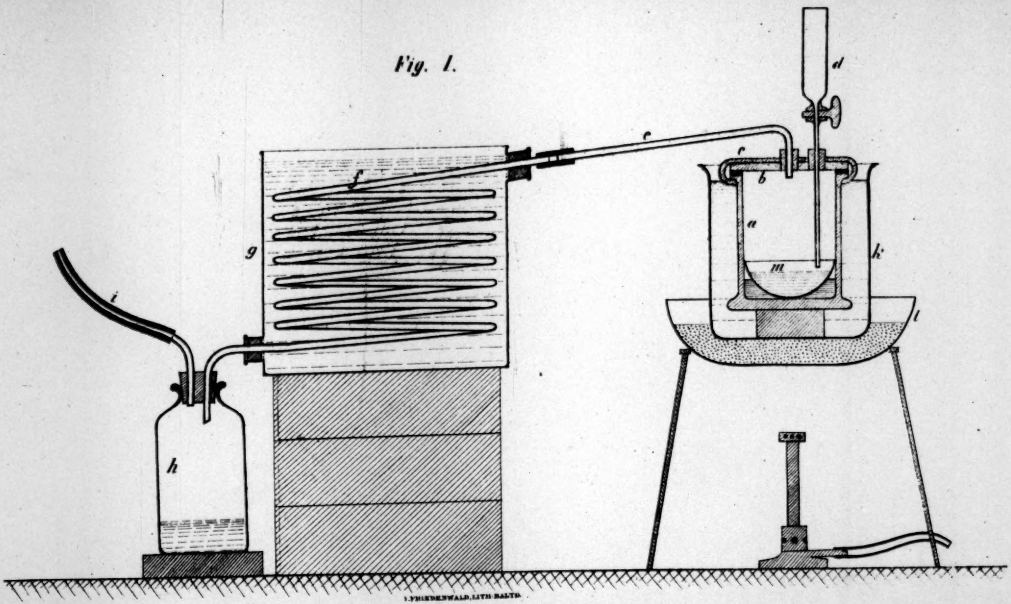
Origin and Character of the Research.

At the close of the report on the extended investigation of the chemical methods heretofore in use for determining organic matter in potable water,[2] certain suggestions were made as to possible improvements in these methods, tending to remedy defects which had been discovered in the course of the research. By direction of the Executive Committee of the National Board of Health, given during the past summer, the most important of these suggested improvements have been practically studied, and the results are now reported upon.

[1] Report on the results of a supplementary investigation, made by the direction of the National Board of Health.

[2] See this Journal, **4**, 241 and 334, and Supplement No. 19 of the National Board of Health Bulletin, May 27, 1882.

Fig. 1.



LITH. BERTHENWALD, LEITH. BALTD.

Combustion Process.

1. *Evaporation of the water under much diminished pressure, in a vessel excluding contact with the atmosphere.*

The apparatus employed for this purpose was arranged as shown in Fig. 1.

The vacuum vessel (*a*) was a tolerably stout glass jar, such as anatomical preparations are kept in, the mouth of which had been ground flat upon a plane surface, and was covered by a disk of thick plate-glass (*b*), with two bluntly tapering holes drilled through it. A strip of thick, hard sheet brass (*c*), having two holes in it corresponding to those in the glass disk, served to form a clamp by which this disk was firmly pressed down upon a ring of sheet India-rubber laid as a washer on the ground mouth of the jar. The holes were fitted with good, soft India-rubber stoppers, through one of which passed a funnel (*d*), with well ground glass stopcock, and tube of almost capillary bore, while through the other passed the glass tube (*e*), serving to carry off the vapor as formed, which tube was connected with the block-tin worm (*f*), surrounded by ice-water in the worm-tub (*g*), and delivered water as condensed into the stout bottle (*h*), from which the thick India-rubber tube (*i*) led to the jet-pump serving to produce exhaustion. The vacuum vessel (*a*) was supported above the bottom of a large glass beaker (*k*) serving as a water-bath, and this in turn was supported on a sand-bath (*l*) above a Bunsen gasburner with "rose" top.

The specimen of water to be examined was evaporated in a glass dish (*m*) of about 4 inches in diameter, placed at the bottom of the vacuum vessel. At first this dish was supported in an upright position by a brass ring, and only touched the glass of the outer vessel at one point at bottom, but it was soon found that with this arrangement the transmission of heat from the water-bath was quite too slow, and hence some mercury was placed in the bottom of (*a*), and the dish was immersed in this to a considerable part of its depth. The jar (*a*) was about 6 inches deep, and of a diameter just sufficient to allow the glass dish to drop down easily, but I should prefer to diminish the depth, and would indeed rather use a simple glass dish, of stout glass, with turned-over lip ground to receive directly the India-rubber washer and plate-glass cover, thus dispensing with the separate vacuum chamber altogether, and

leaving but a single thickness of glass between the water-bath and the water to be evaporated. As my apparatus was arranged, no inconvenience was experienced from vapor of mercury, but in long continued use no doubt enough of this vapor would be given off under the reduced pressure to attack the block-tin worm and make it brittle.

Owing to the slow transmission of heat at the comparatively low temperature employed, the water-bath had to be considerably warmer than the water in the dish within. The bath had immersed in it a thermometer, and was kept filled to the proper height by a constant-level feed, not shown in the figure. The worm-tub was filled with water at the outset, and afterwards fed with lumps of ice; an overflow tube, also not shown in the figure, served to carry off surplus water. If the apparatus were left at work during the night it would become necessary to supply ice-water to the condenser from a large reservoir by a constant-level feed-pipe.

It is desirable that the tubes, both of glass and of block-tin, through which the escaping vapor passes, should have an interior diameter of not less than a third of an inch.

In my experiments the water to be evaporated was introduced, about 50 cc. at a time, by pouring into the wide portion of the funnel (*d*) and very cautiously opening the stopcock. This funnel might, however, be replaced by an almost capillary tube with a glass stopcock upon it, connecting the vacuum chamber with the bottom of a flask containing the whole quantity of water to be evaporated, this flask being placed out of the reach of the heat from the lamp and water-bath; after the temperature and pressure within the apparatus have become approximately constant the stopcock might be set very partially open, so as to allow of continuous supply of more water at just the rate demanded by the progress of the evaporation. In any case the vacuum must be gradually and cautiously established at first, in order to avoid any spattering of the contents of the dish from the escape of bubbles of dissolved gases, and for the same reason each new portion of water must be introduced cautiously, not too much at a time. The stopcock on the inlet tube must be thoroughly well ground, so as to work and remain tight without any lubricant.

The vertical limb of the exit tube for the vapor should be as short as possible, to prevent any risk of liquid water condensing in it and dropping back into the dish, thus producing splashing, and

with the same object in view this short vertical portion of the tube and the whole of the top of the glass covering plate are with advantage to be protected from cooling by some loose cotton-wool. The longer limb of the same exit tube should have a decided downward inclination, so as to prevent any condensed water running back.

Using mercury in the bottom of the vacuum chamber, it was heavy enough to rest steadily on its support, but if this were not the case, and there were a tendency to float up, a simple clamp could of course be used to hold the vessel firmly down.

During the greater part of my work the barometer was at something like 745 mm., and the mercury in the jet-pump gauge stood at about 690–700 mm. Entire freedom from any return of air or water through the pump, and from any abrupt oscillations of the gauge, was secured by an oiled-silk valve, opening only towards the pump, which was inserted in the line of tubing connecting the latter with the evaporation apparatus.

The temperature of the water-bath was so regulated as to keep the water in the glass dish very near, but distinctly below its boiling point for this reduced pressure. The water was therefore evaporated at but little over 30° C., though the thermometer in the water-bath was at 55° or 60°. Of course actual boiling must not be permitted, as it would almost certainly lead to loss of water from the dish.

It was found possible to complete the evaporation of half a litre of water in this apparatus between daylight and dark on a long summer day—say within fifteen hours; but of course the rate of evaporation will depend much upon the more or less free consumption of water in running the jet-pump, so as to steadily maintain a high degree of exhaustion, and the same amount of water may be treated in less time if with higher pressure a higher temperature be permitted.

In order to test the advantage supposed to be obtainable from this method of evaporating water for the combustion process, organic matter had to be introduced in accurately known quantity, and for this purpose leucine and tyrosine were selected, as representing the more stable products of putrefaction liable to occur in natural water, and for which nevertheless the combustion process in its usual form had been found to give results far from satisfactory. Eight experiments were made with each of these substances, using

from 5 to 40 milligrammes per litre of water. The results of the sixteen combustions were as follows:

TABLE I.

	Amount obtained, as percentage on amount originally present.		
	Greatest.	Least.	Average.
Leucine.			
Carbon . . .	97.24	91.40	95.77
Nitrogen . .	95.64	88.27	93.32
Tyrosine.			
Carbon . . .	98.13	92.65	97.04
Nitrogen . .	97.29	90.45	95.72

These figures show a marked improvement upon the results obtained with the same substances by Mr. Noyes, using the Frankland process in its usual form. There is a much nearer approach to the recovery of the quantities of carbon and nitrogen really present in the water as taken for analysis. The two elements are recovered in much more nearly the true proportion to each other. The error for each is in the same direction, that of partial loss, instead of there being a large *excess* of nitrogen. We may fairly conclude therefore that there is real advantage in evaporating the water at the low temperature made available by diminished pressure, and with exclusion of atmospheric air.

It is to be observed, however, that there is uniformly *some* loss, although to a comparatively small extent, so that even for analyses made under these favorable conditions it cannot be rightly claimed that the results represent the whole of the organic matter originally contained in the water. Moreover, it is probable that much of the organic matter occurring in natural waters, and it is certain that some of it, is of less stable character than the leucine and tyrosine experimented on, and for such less stable material larger losses may be expected.[1] And, furthermore, Frankland has found that simple evaporation with sulphurous acid, even at a temperature near 100° C., will not suffice to entirely decompose the carbonates of a natural water, but that active boiling of the water for at least a few seconds after the addition of sulphurous

[1] It has been found by Dietzell (Berichte d. deutsch. chem. Gesellsch. **15**, 551) that during putrefaction very considerable quantities of free nitrogen may be evolved by the formation of nitrous acid and its reaction on leucine, primary amines and ammonia.

acid is necessary ;[1] some injury to the organic matter may be done by such high temperature applied even for so short a time, though the mischief will probably be small. In the experiments just recorded, sulphurous acid, to the extent of about a third of the usual quantity, was added, but the water was not boiled, there being no carbonates present.

Evaporation of the water with magnesia, in order to remove ammonia existing as such or as ammoniacal salts.

Lechartier has advocated[2] the removal of ammonia by evaporation with magnesia, the determination, in the residue, of the nitrogen of organic matter and nitrates, a separate determination of the nitrates, and calculation of the organic nitrogen by difference. It was proposed in my general report to modify this plan by evaporating with magnesia so as to get rid of ammonia, reducing nitrates in the residue brought to a small volume, but not to dryness—as directed by Frankland, by addition of sulphurous acid with a drop of a solution of a ferrous salt and evaporation to dryness, and finally determining organic nitrogen only in the dry residue by combustion.

In investigating this use of magnesia, however, a difficulty was encountered which vitiates Lechartier's method as well as my proposed modification of it. He says that evaporation with magnesia at the temperature of the water-bath, while it completely expels ammonia, does not decompose organic substances, such as urea, and gives in proof of this assertion the results of some experiments, in all of which urea was the only organic substance present. This statement I am unable to verify. I have tried several forms of nitrogenous organic matter liable to occur among the products of putrefaction, and have found that at temperatures no higher than 40° to 50° C. magnesia in the presence of water slowly attacks them, evolving small amounts of ammonia, detectable by litmus paper and paper moistened with the Nessler test solution.

The magnesia was prepared by careful ignition of pure magnesium carbonate, and was very carefully washed to free it from any possible trace of alkali. It was placed, with a few cubic centimetres of water and the organic substance to be experimented on, at the

[1] It might be worth trying whether the decomposition of carbonates could not be advantageously accomplished by some of the acid salts, such as the acid phosphate of calcium, magnesium or sodium.

[2] Comptes rendus, **89**, 231. Ann. de Chim. et de Phys. [V], **19**, 257.

bottom of a short, wide test-tube, the mouth of which was closed by a cork, serving to suspend a strip of the moistened test-paper, and the lower part of the tube was then immersed in a water-bath kept at the required temperature.

Salts of the amines on being thus treated very naturally affected the test-paper at once, and even at common temperature.

Specimens of urea, both of natural and artificial origin, recently recrystallized, gave the reactions of ammonia distinctly and in a very short time at 40° to 45° C. It is stated that the amic acids are not decomposed with evolution of ammonia even by boiling with solutions of the alkalies, but leucine treated as above described with magnesia at 50° C. gave the reactions of ammonia distinctly, though somewhat slowly. Tyrosine behaved in the same way; it seemed to be rather more stable.

Benzamide apparently resisted decomposition, at any rate for some minutes, at 55°, but signs of the ammonia reactions began to appear at 100°.

Hence it appears that magnesia cannot be relied upon to expel pre-existent ammonia only from an evaporated water, leaving nitrogenous organic substances untouched. The long-continued contact with the water as its dissolved contents become concentrated, even at the low temperature made available by lowering of pressure, must produce losses of organic nitrogen, which may very possibly be accompanied by loss of carbon from the same constituents.

It may, however, perhaps be the case that in waters containing relatively very large quantities of ammoniacal salts, the error due to the cause under notice would be less than that attributable to the dissociation of these salts, to an extent not accurately determinable, during the evaporation.

Reduction and removal of nitrates by evaporation of the water with hypophosphorous acid.

In the main report on this water-analysis investigation it was stated that some preliminary experiments made by myself had seemed to show that nitrates and nitrites may be completely reduced by evaporating to a small bulk with no great excess of phosphorous or hypophosphorous acid, guarding against the evolution of phosphuretted hydrogen by the low temperature employed, then adding magnesia in small excess and completing the evaporation, thus leaving the residue in a pulverulent instead of

a sticky condition, easy of removal from the dish, and probably allowing of complete combustion without inconvenience from the final oxidation of the small excess of phosphite or hypophosphite, and without any wrapping up of carbon particles. It was suggested that this plan was deserving of being tested.

It has now been tested, and with satisfactory results so far as the experiments have gone. Solutions of tyrosine, 20 parts per million of water, to which 10 parts of nitrogen per million had been added in the form of potassium nitrate (72.2 parts of this salt), were evaporated with 2 to 5 cc. of a moderately strong solution of hypophosphorous acid. The highly concentrated, but not yet dry, residues were carefully tested for the nitrate by means of brucine, and for nitrite by Griess' naphthylamine reaction, but negative results were obtained as to both. There was no darkening, or other apparent indication of the tyrosine being attacked, and on adding magnesia in excess, as proposed, to residues from the evaporation of similarly treated solutions and completing the drying, the combustion in the Sprengel vacuum was carried out without any special difficulty. In a natural water the carbonates present would be decomposed by the hypophosphorous acid, and carbon dioxide would be expelled during the evaporation.

In applying this method, using magnesia to neutralize the excess of acid and to dry up the residue to a condition in which it can easily be removed from the dish and mixed with cupric oxide, care must of course be taken that the magnesia is thoroughly ignited before being used, that it is not exposed to any considerable extent to the air after it has been so prepared, that the evaporation is carried on in such a vacuum chamber as has been described, and that the dried residue is not for any needless length of time exposed to the atmosphere before introduction into the combustion tube. Neglect of these precautions would lead to absorption of carbon dioxide, and consequent vitiation of the results as far as carbon is concerned. To avoid, however, the difficulty which had been ascertained to exist, arising from the action of magnesia on nitrogenous organic matter, it was thought best to use barely enough magnesia to neutralize the excess of acid, and to complete the drying up with an addition of pure *silica*, prepared by ignition of silicic acid, itself made from silicon fluoride. With this modification of the plan proposed the combustion gave results for the carbon and nitrogen of the tyrosine

as good as those obtained on the average from the solutions of this substance in pure water without additions.

The solution of hypophosphorous acid should be carefully guarded from the air, and its strength ascertained from time to time (in order to judge approximately of the quantity to be used), not by neutralization, but by the reducing action upon a solution of mercuric chloride.

Albuminoid-Ammonia Process.

The examination of modified forms of this process was undertaken by Dr. Charles Smart, U. S. A., who has furnished the following statement of results obtained. The appointment of Dr. Smart to the office of Secretary to the National Board of Health, and the pressure of duties thus entailed upon him, have prevented the whole plan of experiments intended being carried out, but the main points on which information was sought have been covered.

"The experiments detailed below were intended to determine the conditions under which ammonia in small quantities is evolved from its containing liquid, and those under which perfect condensation or absorption may be subsequently obtained.

Series of Experiments on the Liberation and Condensation of minute quantities of NH_3.

The charge for distillation consisted of so many cc. standard NH_3 solution (1 cc. = .01 mgrm. NH_3) + so many of ammonia free water, making a total of 500 cc.

A. 1 mgrm. NH_3, ordinary distillation. Temperature of distillate 27° C.

.50 .21 .055 .01 = .855 = 14.5 per cent. loss.

Compare with H and I.

B_1. .5 mgrm. NH_3, ordinary distillation. Temperature of distillate 28° C. Temperature in retort 101° C.

.40 .06 .005 = .465 = 7 per cent. loss.

B_2. 1 mgrm. NH_3. Conditions as in B_1.

.76 .10 .01 .00 = .87 = 13 per cent. loss.

Compare with A in which gas-jet was smaller and time of distillation longer.

B_3. 2 mgrms. NH_3.

1.34 .32 .05 .015 .00 = 1.725 = 13.75 per cent. loss.

C_1. 1 mgrm. NH_3, receiver closed by sulphuric acid bulbs, connected with water-jet, tension reduced six inches; retort heated in vessel of boiling water. Temperature in retort 95° C., of distillate 28° C. Distillation slow (90 minutes for 50 cc).

.46 .28 .14 .035 .015 with .01 in acid = .94 = a loss of 6 per cent.

C_2. 2 mgrms. NH_3. Temperature in retort 96° C.; other conditions as in C_1.

.77 .56 .27 .12 .06 .025 with .035 in acid = 1.84 = a loss of 8 per cent.

D_1. .5 mgrm. NH_3. Conditions as in C, but flame applied to retort. Temperature in retort 97–97.5° C., of distillate 28° C. Distillation rapid (12 minutes for 50 cc).

.36 .075 .01 with .02 in acid = .465 = a loss of 7 per cent.

D_2. 1 mgrm. NH_3.

.72 .20 .035 .015 with trace in acid = .97 = a loss of 3 per cent.

D_3. 2 mgrms. NH_3.

1.41 .36 .05 .01 and trace only in acid = 1.83 = a loss of 8.5 per cent.

E_1. .5 mgrm. NH_3, ordinary distillation, but receiver closed by sulphuric acid bulbs. Temperatures 101° and 28° C.

.37 .075 .015 with .02 in acid = .48 = a loss of 4 per cent.

E_2. 1 mgrm. NH_3.

.72 .19 .035 .005 with .02 in acid = .97 = a loss of 3 per cent.

E_3. 2 mgrms. NH_3.

1.39 .34 .07 .01 with .03 in acid = 1.84 = a loss of 8 per cent. Compare E with B_1.

F_1. 1.5 mgrm. NH_3. Conditions as in E, but pure water in bulbs instead of sulphuric acid.

1.12 .20 .02 .005 = 1.345 = 10.3 per cent. loss.

G_1. .5 mgrm. NH_3. Conditions as in F, but with water-flask as guard beyond the water-bulbs.

.37 .07 .015 = .455 = a loss of 9 per cent.

G_2. 1 mgrm. NH_3.

.72 .18 .03 .0025 and trace in bulb = .9325 = 6.75 per cent. of loss.

G_3. 2 mgrms. NH_3.

1.41 .32 .065 .01 with trace in water = 1.805 = a loss of 9.75 per cent. Compare G with E and B.

H_1. .5 mgrm., ordinary distillation. Temperature of distillate 6° C.

.40 .08 .02 .00 = .50

H_2. 1 mgrm. as in last.

.80 .14 .03 = .97 = loss of 3 per cent.

H_3. 1 mgrm. as in last.

.80 .15 .03 = .98 = loss of 2 per cent.

I_1. .5 mgrm. condensed in coil 18 feet long. Temperature of distillate 6° C.

.08 .32 .08 .015 .005 = .50

I_2. 1 mgrm. as last.

.43 .38 .12 .04 .01 = .98 mgrm. = loss of 2 per cent.

I_3. 1 mgrm. as last.

.35 .40 .12 .07 .03 = .97 mgrm. NH_3 = loss of 3 per cent.

Second Series of Experiments on the Liberation and Condensation of minute quantities of NH_3 from Water.

I. .5 mgrm. NH_3, in a retort connected with a water-jet pump, no condenser, but sulphuric acid bulbs between retort and pump, 6½ inches pressure removed; stream of air passing through apparatus entering by means of a glass wool filter moistened with sulphuric acid. Temperature 28° C. After 24 hours .11 mgrm. NH_3 was found to have left the retort for the acid bulbs.

II. .5 mgrm. NH_3, apparatus as in I, but temperature in retort kept at 63° C. At end of 21 hours, 190 cc. of the water were found to have passed into the acid bulbs and flasks carrying with them all of the NH_3.

III. .5 mgrm. NH_3, apparatus as last. Temperature in retort 55° C. At end of 18 hours, 85 cc. were found to have passed over carrying with them .488 mgrm. NH_3.

IV. As last. At end of 6 hours, 31 cc. had passed over with .29 mgrm. NH_3.

V. As last, but with the air drawn *through* the liquid to cause an artificial ebullition. At the end of 5 hours, .27 mgrm. was found in the acid.

VI. As last, but with 9 inches pressure removed. Temperature 50° C. At the end of 16 hours, 60 cc. had come over bringing all the NH_3.

VII. As last. At end of 4 hours the 10 cc. which had come over contained only .25 mgrm. NH_3.

VIII. As last, but with 10½ inches pressure removed. Temperature 49° C., and 6½ hours of exposure, 13 cc. passed over containing .27 mgrm. NH_3.

Experiments on the Decomposition of Urea during Distillation of the Water holding it in solution.

The urea used in these experiments contained .45 per cent. of free NH_3. This amount must be deducted from the first recorded results of every experiment.

1st. 10 mgrms. urea (containing .045 mgrm. NH_3) in 500 cc. water distilled from water-bath, and with 6½ inches pressure removed from interior of apparatus. Temperature in retort 96° C. Two hours required for the distillation of each measure of 50 cc.

Result 1st measure .19 mgrm.
2d " .37 "

2d. 10 mgrms. urea, but without the water-bath and jet-pump. Distillation rapid. 12 minutes for 50 cc.

1st measure .12 mgrm.
2d " .10 "

3d. 20 mgrms. (containing .09 mgrm. NH_3) operated on as in experiments I, II, III, &c. At end of 5 hours, 40 cc. had passed over carrying with them .19 mgrm. NH_3 into the acid.

4th. 20 mgrms. urea were permitted to remain under the influence of the jet-pump and passing air current as in I for 40 hours; .14 mgrm. was found in the acid.

5th. 20 mgrms. were exposed in solution to the air for 40 hours, and at the end of that time showed the presence of .09 mgrm. NH_3 as when freshly dissolved.

6th. 20 mgrms. at 60° C. and 6½ inches for 7 hours gave .20 mgrm. NH_3 in 40 cc. which passed over into the acid bulbs.

7th. 20 mgrms. at 60° C. and 6½ inches for 16 hours gave in 65 cc. distilled .25 mgrm. = .16 mgrm. when the .09 free NH_3 is deducted.

8th. 35 mgrms. urea (containing .16 mgrm. NH_3) at 55° C. and pressure as in last gave after 16 hours 67 cc. containing .29 mgrm. NH_3.

9th. 35 mgrms. urea as in last, but with only 6 hours exposure, gave .035 mgrm. in 26 cc. distilled. This .035 represents the decomposition effected during the time, as the residue from 8 was used and it was free from the original ammonia taint of the urea.

10th. The residue from 9 treated as before for 16 hours gave .09 in the 70 cc. which passed over.

A comparison of C and D shows that water containing a trace of ammonia may be heated within a degree or two of its boiling point without any rapid evolution of the ammonia, but that as soon as the extra degree or two needful to cause ebullition has been added, the ammonia passes over rapidly with the watery vapor. Ninety minutes of a heat just below the boiling point are required to accomplish what may be effected in twelve minutes if that point is attained. A reduction of pressure on the surface of the liquid promotes the evolution, by causing ebullition at a lower temperature; compare D with E. A diminished pressure no doubt acts at all temperatures in aiding the evolution; and a weak solution as in I may lose its ammonia at ordinary temperatures, but the length of time required to effect this renders the process valueless as a practical method. Nevertheless, by increasing the temperature under the lessened pressure the time required may be so reduced as to give the process a value in practice.

As the rapidity of the evolution of the ammonia from the water containing it depends mainly on the presence of heat sufficient to boil the water, so a perfect condensation, where heat has been applied to cause rapid evolution, can only be obtained by the needful reduction of temperature; compare the whole series A, B and C with H and I. Where the condensing liquid runs freely from the tap through the condenser so as to give the distillate a temperature a few degrees above the freezing point, the ordinary condenser is as efficient as one with a condensing tube many times longer; compare H and I.

But where the liberation of the ammonia is effected slowly under reduced pressure and at temperatures considerably below the boiling point, the whole may be recovered by absorption in acid without the aid of a condensing circulation. See experiments II, III, and VI.

As with the evolution of ammonia, so with the decomposition of urea: it is effected slowly at temperatures below the boiling point, but as soon as that point is reached the ammonia from its dissolution is given up rapidly. Compare experiment 2 with the others of that series.

Practically it may be said that where we are dealing with free ammonia and non-volatile and stable organic matter in a water, the ordinary process with a condensing medium which gives a proper temperature to the distillate may be considered satisfactory.

But where we have to discriminate between free ammonia and urea, the slower method by absorption in acid under reduced pressure may be of value. The experiments 3–8 show that if the operation is commenced in the afternoon and permitted to continue until next morning, the whole of the ammonia may be expected in the acid bulbs, and this may be assumed with greater certainty if more than one-tenth of the liquid has distilled in the meantime; but if the operation is commenced in the morning or forenoon, it is doubtful if it can be completed in the ordinary working hours of the laboratory. Experiments 7–10 indicate that during this liberation of the free ammonia present, the urea which may accompany it will only suffer decomposition to the extent of from three to eight tenths of one per cent.

CH. SMART, *U. S. Army.*"

PERMANGANATE PROCESS.

Maintenance of an approximately constant excess of permanganate during the progress of action on the organic matter in a sample of water.

The effect of thus modifying the permanganate process as described and used by Tidy was tested as follows: The process was first applied in its usual form to water artificially polluted with organic matter,[1] extending, however, the time of action to 24 hours, and making determinations in separate flasks of the oxygen consumed at the end of 1, 3, 6, 9, 12 and 24 hours respectively. Enough of the organic matter was used to consume altogether a large proportion of the oxygen of the charge of permanganate. Having plotted off a curve on paper representing the rate of consumption of the oxygen as thus found, it was determined how much additional permanganate should be added at the end of each half-hour for the first three hours, at the end of each hour for the succeeding nine hours, and at the end of each six hours for the remaining twelve hours, in order to maintain as nearly as these intervals would permit, a constant excess throughout the whole period. These additions were made at the proper times to a new lot of the polluted water altered only by keeping for one day, and determinations were made as before of the oxygen consumed at the end of 1, 3, 6, 9, 12 and 24 hours.

[1] An infusion of dead forest leaves and the drainings from a pile of animal manure were the polluting materials used.

Results a little higher were obtained by this modified process as compared with those given by the former method. The difference, however, was not very great. The chief evidence of greater regularity of action was furnished by experiments, made simultaneously, on two different dilutions of the same solution of organic matter. These gave results as to oxygen consumed which were almost exactly in proportion to the difference of strength when the modified process was used, whereas the stronger solutions gave somewhat lower results than would have been calculated from those for the weaker dilutions when the original form of the process was applied. These comparative experiments were too few in number to generalize from with much positiveness, but they may fairly be taken, as far as they have gone, in confirmation of the soundness of the principle on which the suggested improvement is based.

ON THE ACTION OF CERTAIN VEGETABLE ACIDS ON LEAD AND TIN.

By Francis P. Hall.

The enormous and continually increasing use of canned goods—fruit, vegetables, meat, etc.—has led to the discussion, on sanitary grounds, of the possible injurious effect of the material of the can on its contents; and, among other chemical questions, is that of the effect of various vegetable acids upon the material of the cans, *i. e.* upon the can itself and upon the solder which may be exposed on the inside. The fear also has arisen lest the tin-plate itself of which the cans are made should, for the sake of greater cheapness, be made not with pure tin, but with an alloy of lead and tin.

The following paper contains the results of experiments on the action of certain acids on tin and on alloys of tin and lead, and also the results of some investigations as to the quality of the tin-plate and tin-foil in actual use as envelopes for food products.

On the Action of Vegetable Acids on Alloys of Lead and Tin.

One of the most important things to be considered in investigating the power of an alloy to resist corrosion is the electrical

relation of the metals which compose it. Lead and tin are so nearly alike in this respect that their relation to each other may be reversed in different liquids, or even in the same liquid under different circumstances. On this subject chemical literature contains many and quite discordant statements. It seems, however, to be fully established by the experiments of Weber[1] that ordinary vinegar will dissolve lead from an alloy of lead and tin containing only 5 per cent. of lead, and further, that from a dilute acidulated solution of acetate of lead, lead is precipitated by an alloy containing as little as 5 per cent. of tin.

In the following investigation I wished to ascertain quantitatively the action of several of the more common vegetable acids, all quantitative experiments that I had seen being made with acetic acid only.

To ascertain definitely the effect of alloying on the corrosion of the metals, the amount of lead or tin dissolved when pure must be compared with the amount dissolved, under the same conditions, from an alloy exposing the same surface of the metals in question. To make the experiment, as is usually done, with equal-sized pieces of pure metal and alloy is not fair, if we consider the action to be proportional to the surface of metal exposed, because then the united surface of the two pieces of pure metal is twice that of the alloy and the surface of either metal exposed in the alloy is less than that exposed by the piece of pure metal.

To overcome this difficulty I proposed to proportion the size of the pure metal plates according to the composition of the alloy. In order to proportion them more easily and to have them of a size readily comparable with one another, I took into account the specific gravity of the metals in making the alloys. Hence, barring the unequal contraction of the metals on alloying, I had alloys exposing a known surface of lead and tin. I could now expose an equal surface of pure metal to the same acid under the same conditions and compare the action, thus getting a fair idea of the effect of alloying the metals, as well as the action of the acid on a known surface of pure lead or tin.

I made after this plan three alloys—one with equal parts of lead and tin, one with an excess of lead, and one with an excess of tin. These were all that I had time to experiment with, but the researches

[1] Dingl. pol. Jour. **232**, 153, 264; Wagner Jahresb. 1879, 196-207.

of Weber[1] show that, for acetic acid at least, the action on the alloys increases quite regularly as the proportion of lead increases, therefore the action on alloys containing lead and tin in different proportions than those I took can be inferred with fair accuracy by interpolation.

The alloys were made from pure lead and tin, well stirred when melted, then cast in thin sheets in iron moulds. Afterwards these sheets were rolled into thin strips and trimmed to the size desired. Strips of pure lead and tin were made at the same time. The tin used was Banca tin, containing 99.78 per cent. of tin, a trace of lead and a trace of copper.

For acids I used a solution of glacial acetic acid in distilled water, which, on titration with a standard solution of ammonia, proved to have a strength equal to 5.75 per cent. of acetic acid; also solutions of crystallized tartaric and citric acids, which neutralized the same amount of ammonia.

The tartaric and citric acids contained, as they always do, a trace of lead, but the amount was much too small to appreciably influence the results.

Strips of the alloys 1.2 inch wide and 12 inches long were cut out, exposing, therefore, counting both sides, 28.8 square inches or one-fifth of a square foot. Pieces of pure lead and tin were taken of the same width, but varying in length to suit the composition of the alloy to which each corresponded. These strips of metal were rubbed until perfectly bright, washed with a little dilute alcohol, heated in a drying closet, and when cool weighed. Immediately after weighing they were put into separate beakers each containing 200 cc. of acid. The long strips were coiled and kept off the bottom of the beaker by a $\bigvee$ of glass rod. In each case the liquid covered the metal by more than an inch, so that the air did not take part directly in the action. Each beaker was covered with a watch-glass.

After standing for two weeks in a place where the temperature varied from 25° to 35° Centigrade, the contents of the several beakers were examined. The most notable change was that the acid containing the tin, as well as that containing the alloys, had a decided yellowish tint, while that containing the lead was perfectly clear and colorless. The metal in all cases was more or less tar-

[1] *Loc. cit.*

nished, but the tin much more noticeably so than the lead. Two of the alloys in the acetic acid were sprinkled with little black crystals. These crystals were evidently metallic; they were carefully collected, washed with alcohol, dried and analyzed. The result of the analysis is given later. The smallest of the pieces of lead in the tartaric acid was covered with small transparent crystals; these were set aside for further examination. The pieces of tin were covered with a dusty powder, but there was not enough of it to analyze.

When the contents of each beaker had been carefully examined, the strips of metal were lifted out, washed with a jet of water, dried with a soft towel, and, after remaining a while in a drying-closet, weighed. The loss of weight served as a rough check on the subsequent analysis of the solutions. Next, the metal in solution was precipitated by sulphuretted hydrogen. The lead caused dense black precipitates, much finer in the tartaric and citric acid than in the acetic. The tin in the acetic acid came down of a dark brown color, showing the stannous salt, while that in the tartaric acid gave, at first, merely a yellow coloration. After standing some time, however, a flocculent, apparently hydrated precipitate settled out. The same seemed to be the case with the citric acid solutions, but on closer examination an almost transparent precipitate could be seen, and it settled much quicker than in the case of the tartaric acid. These same peculiarities of the precipitates of sulphide of tin were noticed throughout the whole investigation. It was also invariably the case with the alloys that the precipitates in acetic acid were dark brown, while those in tartaric and citric acids were light-colored and flocculent.

After some experimenting I found the best way to separate the sulphides of lead and tin in the solutions was to carefully decant as much as possible of the liquid through a filter, neutralize what remained with ammonia water, add a little yellow ammonium sulphide, and heat; then collect the sulphide of lead on the filter used before. The tin was determined in the alkaline filtrate. The sulphide of lead was converted into the sulphate before weighing; the sulphide of tin into the oxide in the usual manner. In no case was either metal determined by difference.

The results obtained are given in the following tables. The first two columns of Table I give the amount of surface of each metal exposed both as pure metal and in the alloy.[1] The last two give the total weight of metal, lead and tin, dissolved from the alloy, and from an equal surface of the same metals exposed in the pure state. But although the surface exposed was the same, the unalloyed metals were exposed to twice as much acid, each being in a separate beaker with 200 cc. of the acid. This might have been righted by proportioning the acid to the surface exposed, but this did not occur to me until too late. It will be noticed how often the amount dissolved when unalloyed is equal to twice that dissolved from the alloy.

TABLE I.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight, in grams.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic ...	7.2	...	100.	...	0.4320	0.4216	...	...	...	...	...
" ...	7.2	21.6	34.1	65.9	0.4525	0.0432	0.3312	11.54	88.46	0.3744	0.7122
" ...	...	21.6	...	100.	...	...	0.2906	...	...	...	...
" ...	14.4	...	100.	...	0.5470	0.5444	...	...	...	...	...
" ...	14.4	14.4	60.8	39.2	0.5145	0.0558	0.3552	13.57	86.42	0.4110	0.8242
" ...	...	14.4	...	100.	0.2820	...	0.2798	...	...	...	...
" ...	21.6	...	100.	...	0.6195	0.6137	...	...	..	...	...
" ...	21.6	7.2	80.84	19.16	0.6570	0.4887	0.1589	75.46	24.54	0.6476	0.8073
" ...	...	7.2	...	100.	0.2135	...	0.1936	...	...	...	...
Tartaric.	7.2	...	100.	...	...	0.0452	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0280	0.0029	0.0269	9.73	90.27	0.0298	0.0664
"	...	21.6	...	100.	0.0210	...	0.0212	...	...	...	...
"	14.4	...	100.	...	0.6605	0.0586	...	...	...	...	...
"	14.4	14.4	60.8	39.2	0.0385	0.0042	0.0332	11.23	88.77	0.0374	0.0750
"	...	14.4	...	100.	0.0150	...	0.0164	...	...	...	...
"	21.6	...	100.	...	0.0655	0.0654	...	...	...	...	...
"	21.6	7.2	80.84	19.16	0.0345	0.0080	0.0269	22.92	77.08	0.0349	0.0787
"	...	7.2	...	100.	0.0115	...	0.0113	...	...	...	...
Citric ...	7.2	...	100.	...	0.3540	0.3521	...	...	...	...	...
" ...	7.2	21.6	34.1	65.9	0.1690	0.0165	0.1461	10.15	89.85	0.1626	0.4785
" ...	...	21.6	...	100.	0.1175	...	0.1264	...	...	...	...
" ...	14.4	...	100.	...	0.4355	0.4348	...	...	...	...	...
" ...	14.4	14.4	60.8	39.2	0.1725	0.0210	0.1355	13.42	86.58	0.1565	0.5439
" ...	...	14.4	...	100.	0.1080	...	0.1111	...	...	...	...
" ...	21.6	...	100.	...	0.4870	0.4875	...	...	...	...	...
" ...	21.6	7.2	80.84	19.6	0.2305	0.0982	0.1221	44.58	55.42	0.2203	0.5946
" ...	...	7.2	...	100.	0.1030	...	0.1071	...	...	...	...

[1] See page 441.

The alloys Nos. 1 and 2 in the acetic acid were the ones on which the small black crystals before mentioned were found. The crystals on No. 1 weighed 0.0970 gram, and gave on analysis 0.0931 gram of lead, or 91.6 per cent. Those on No. 2 weighed 0.0620 gram, and gave 0.0586 gram of lead, or 94.45 per cent. They were evidently, therefore, crystals of lead. This amount of lead might have been considered as having been in solution, but it is not included in the amount given in the tables. Weber[1] noticed similar crystals in his experiments, and explained their presence by supposing that, at the surface of the liquid where the oxygen of the air and the acid both acted on the metal, so much lead was dissolved that it was precipitated again by the tin of the alloy below the surface. As, in my experiments, the metal was kept entirely covered by the acid, this could hardly have been the case.

The transparent crystals found on the smallest piece of lead in the tartaric acid were nearly, if not quite, insoluble in water. Under the microscope they appeared to be hexagonal and very much like small quartz crystals. They were found, on comparison, to have the same form as crystals of tartrate of lead. From this and from a few qualitative tests I decided that they must be tartrate of lead. The crystals adhered so firmly to the lead that they could not be removed, therefore the loss of weight, as well as the lead in them, could not be determined.

The results of the experiment agree in all essential points with those statements which I have found that have been supported by actual experiment. Those statements which would have us suppose that alloying with tin increased the corrosion of lead seem to be founded on the case of some stray tank or pipe, rather than on a well-conducted research. Moreover it does not appear, as is often supposed to be the case, that the alloy is more acted upon than either of the metals.

It was suggested that the galvanic action would influence more the rapidity of the corrosion than the total amount of metal dissolved; hence that the effect would be more clearly marked at the end of two days than at the end of two weeks, but experiment showed that this is not the case. For this experiment I used only one of the alloys, namely that containing the most tin: the results are recorded in Table II. While the amount of action is

[1] *Loc. cit.*

not exactly proportional to the time of exposure, it is not far from being so in the case of acetic acid, and in the case of citric and tartric acids it is evident that the action is very slight at first and increases appreciably as time goes on.

TABLE II.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight, in grms.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead.	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic	7.2	...	100.	..	0.0515	0.0497	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0460	0.0046	0.0387	10.62	89.38	0.0433	0.0896
"	...	21.6	...	100.	0.0400	...	0.0399	...	...	...	...
Tart'c	7.2	...	100.	...	0.0400	0.0374	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0120	0.0012	0.0124	8.82	91.82	0.0136	0.0470
"	...	21.6	...	100.	0.0255	...	0.0096	...	...	...	...
Citric	7.2	...	100.	...	0.0625	0.0599	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0215	0.0015	0.0218	6.44	93.56	0.0233	0.0817
"	...	21.6	...	100.	0.0120	...	0.0218	...	...	...	...

In these experiments, although the metal was covered with the acid and the beaker with a watch-glass, the air had more or less free access to the surface of the liquid. To see what effect the air had on the corrosion, and to approach more nearly the conditions of a sealed can, I took some glass-stoppered bottles and repeated the experiment in them. I weighed the strips of metal as before and placed them in the bottles, then heated the bottles on steam cups, and while hot filled them with the acid, also heated to boiling to expel any air. The bottles were at once tightly stoppered. As they cooled a few of them leaked a little, but as they were nearly full of liquid very little air could enter. They were put in the same place as in the former experiments and left for two weeks. On being examined at the end of this time there was evidently much less corrosion than in the case of the corresponding experiments in open beakers. There was no discoloration, and no crystals formed. That the air had been pretty well excluded could be seen from the way the stoppers stuck in the bottles even after they could be turned with ease. The same difference in the character of the precipitates of sulphide of tin was noticed as before.

The following table gives the results:

TABLE III.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight in grams.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead.	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic	7.2	...	100.	...	0.0900	0.0886	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0365	0.0052	0.0289	15.25	84.74	0.0341	0.1332
"	...	21.6	...	100.	0.0430	...	0.0446	...	...	...	...
Tart'c.	7.2	...	100.	...	0.0365	0.0343	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0085	0.0018	0.0084	17.65	82.35	0.0102	0.0400
"	...	21.6	...	100.	0.0080	...	0.0057	...	...	...	...
Citric.	7.2	...	100.	...	0.0560	0.0510	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0250	0.0018	0.0249	6.74	93.25	0.0267	0.0644
"	...	21.6	...	100.	0.0120	...	0.0134	...	...	...	...

It will be noticed that the corrosion was considerably less. For convenience I give a table showing the comparative results obtained in open and in closed vessels.

TABLE IV.

Dissolved from	By Acetic Acid.		By Tartaric Acid.		By Citric Acid.	
	Open.	Closed.	Open.	Closed.	Open.	Closed.
Lead	0.4216	0.0886	0.0542	0.0343	0.3521	0.0510
Alloy	0.3744	0.0341	0.0298	0.0102	0.1628	0.0267
Tin	0.2906	0.0446	0.0212	0.0057	0.1264	0.0134

The acids used were of about the strength of good vinegar. It would naturally be supposed that less strong acids, such as usually occur in canned goods, would cause correspondingly less corrosion. This does not seem to be the case; an incomplete series of experiments seem to indicate that a dilute acid, if used in sufficient quantities, causes much more corrosion than would be inferred from its strength.

To try now the action on the cans themselves, and also the effect of the solder, I took three cans that had been emptied and put 200 cc. of acid into each—acetic acid in one, tartaric acid in another, and citric acid in the third. I covered these cans as well as I could by tying two thicknesses of paper over each, but of course they were practically open cans; moreover, the acid did not nearly fill them. They would represent, therefore, a can that had been partly emptied and set away, rather than a fresh one.

When examined at the end of two weeks, the tinning up as far as the acid reached was entirely taken off, except in the acetic acid. The citric acid had a yellowish color, and a quantity of white powder was deposited on the bottom of the can. I emptied the acid from the cans and added a few drops of chlorhydric acid, fearing that the organic acid was not sufficient to hold up the sulphide of iron. The addition of chlorhydric acid and a little warming dissolved the white powder in the citric acid, and at the same time destroyed the yellow color. On passing sulphuretted hydrogen through the solutions, a very large precipitate was obtained. This I filtered off, washed, and treated with ammonium sulphide; the residue was collected on a filter, dissolved in strong chlorhydric acid, and after evaporation the lead was precipitated as sulphate.

The tin was determined in the ammonium sulphide solution. The result was as follows:

Acetic	acid dissolved	0.4178	gram of	tin and	0.0117	of lead
Tartaric	"	"	1.0430	"	"	0.0873	"
Citric	"	"	0.6828	"	"	0.1559	"

In addition to the lead and tin there was a good deal of iron dissolved.

This shows that corrosion takes place very rapidly after a can is opened, and that a can once opened should be emptied at once. One would have supposed that the acetic acid would have acted more than the others, and it probably would if the conditions in the different cans had been exactly the same. It is probable that more solder was exposed in the cans treated with tartaric and citric acids; at any rate the lead must have come from the solder, as the tin from which the cans were made proved, on being tested, to be free from lead.

On the Quality of Commercial Tin-plate.

Having seen the action of some of the more common vegetable acids on lead and tin, and the alloys of the same, we come to the tin-plate itself.

The tin-plate used in this country is entirely imported, most of it coming from England. The two principal kinds are "Bright plate" and "Terne plate." Bright plate is, or should be, tinned only with pure tin. It is divided into several grades, according to the thickness of the tinning and the quality and heaviness of the

iron which forms the basis, but in all these grades the tinning is supposed to be pure tin. Terne plate, on the other hand, is known to contain large quantities of lead, and is often called lead-plate, there being no attempt to pass it for tin, at least by respectable persons.

Tinware and fruit-cans are made from bright plate, while terne plate is used altogether for roofing. Of course the boundaries are sometimes overstepped; those who are very particular use bright plate for roofing, and those who are too avaricious may make tinware out of terne plate. This last, I think, however, is very seldom the case, and the heavy nature of terne plate unfits it for canning.

Knowing these divisions of tin-plate, the questions before us now are: Is bright plate, especially that used in canning, always tinned with pure tin? and how commonly is terne plate used where it will come in contact with food?

I procured some specimens of plate through the kindness of one of the largest importing houses in the city. These I tested by several methods. With the bright plate, taking small pieces, I could find no lead at all, and only after taking half a square foot did I find a trace. This was no more than would be found in most English bar-tin. I now tested a number of cans from various sources, as well as the worst-looking tinware from the so-called 5-cent stores, but not once did I find enough lead to show an intentional adulteration. Neither have I found any well instituted attack on the character of the tin-plate in this country. A good deal has been said and many suspicions thrown out, but the only statements of analyses that I have seen are in a Board of Health report of a Western State.[1] The author found lead so invariably in all tin articles that came into his hands that one cannot help suspecting that the methods of analysis were unreliable. He even observes that he found a considerable quantity of lead in what was sold for pure tin—a thing quite possible, it is true, but not likely to happen with dealers to whom a chemist would naturally go for pure supplies.

Even if the tin of the can is pure, there remains the solder, which always contains a large quantity of lead, and is used very freely. There remains, also, the fact that the vegetable acids act considerably upon tin itself. There are many published statements as to the presence of tin in canned goods, and the careful inspection of

[1] Mich. Board Health Rept. 1878, p. 29.

the inside of a can which has contained an acid fruit shows quite clearly in many cases that corrosion has taken place. Moreover, although my experiments tend to show that the amount dissolved when the air is excluded is much less than when open, still it is an appreciable quantity; and if, as seems to be the case, the amount increases with the time, that dissolved from an old can must be considerable.[1]

The terne plate, which is that most often used for roofing, cannot be considered quite harmless in cases where the water from the roof is used for household purposes. But as the tin roof as well as the whole house is generally covered with a paint containing far more lead than the terne plate itself, it would be absurd to complain while we use white lead to such an extent as at present.

I made a rough analysis of the tinning of terne plate by dissolving it off with chlorhydric acid, precipitating the lead and tin as sulphide and separating them with sulphide of ammonium. The result was as follows: One-fifth of a square foot gave 1.1650 gram of lead and 0.4469 gram of tin, which would make the tinning consist of 72.27 per cent. of lead and 27.73 per cent. of tin. Terne plate can be readily told by its dullness; it comes also in larger sheets than bright plate.

Although constantly on the watch for tinware made of terne plate, I have been able to find none. I am informed on good authority, however, that it is sometimes used for that purpose, but conclude that such use must be rare in this section of the country.

On Commercial Tin-foil.

Tin-foil is so much used now-a-days on chocolate, compressed yeast, cheese, and the like, that I thought the analysis of a few samples might not be amiss. Here at the outset we have a good proof of adulteration, from the fact that the price of most foil is but little more than half the price of pure bar tin.

I collected a number of samples from different importers and manufacturers. They varied greatly in thickness, coloring, and design, but I had reason to suppose that many were the same in composition. I took what I thought was a fair sample of them as regarded composition, and analyzed them.

The method used was that usually used for solders, the oxida-

[1] It is hardly to be supposed that the proportion indicated by the above experiments continues indefinitely.

tion with nitric acid. It was not thought necessary to correct for the trace of lead retained by the oxide of tin; neither were traces of copper or other metals sought for, which even if present would hardly influence the character of the foil, at least as far as sanitary purposes were concerned. The results of the analyses will be found in Table V. I give in the table the size of the piece of foil taken for analysis, its weight, and the weight of the lead and tin found in it, as well as the percentage composition. Only the first three foils were sold for pure tin. Some were sold as "composition foils," but generally, unless special inquiry was made, nothing was said of their composition.

TABLE V.

No.	Amount taken		Amount found in grams.		Percentage.	
	Size in sq. in.	Weight in grams.	Tin.	Lead.	Tin.	Lead.
1	6	0.2285	0.2275	...	99.53	...
2	6	0.4260	0.4227	...	99.23	...
3	6	0.5950	0.5929	...	99.65	...
4	6	0.5150	0.1162	0.3945	22.56	76.60
5	6	0.9080	0.0902	0.8152	9.94	89.95
6	6	0.7140	0.1642	0.5464	23.00	76.41
7	6	2.0785	0.0839	1.9860	3.86	95.75
8	6	1.8580	0.1172	1.7360	6.31	93.43
9	6	0.3030	0.1125	0.1819	37.44	60.03
10	2.25	0.4720	0.1078	0.3678	22.84	77.94
11	3	0.8005	0.2004	0.5969	25.03	74.55
12	6	1.4940	...	1.2240	...	81.92

In order to see if I had had a fair sample of the foils in general use, and to see which of them were most used on articles of food, I took several foils that had been in actual use and analyzed them. The results appear in Table VI. It will be seen that each corresponds very nearly to some one in Table V. Nos. 21, 23 and 28 were on chocolate; Nos. 22 and 27 on different kinds of compressed yeast; Nos. 25 and 26 on "Neuchâtel" cheese; No. 24 on the outside of a box of troches. No. 23 was on a small cake of chocolate bought at a street stand, while No. 28 was an embossed foil and on a very fashionable cake of chocolate. No. 25 was very brittle and showed signs of being acted upon. The cheese was quite acid to litmus.[1]

[1] The use of a foil containing about 75 per cent. of lead for wrapping the so-called Neuchâtel and other soft cheese is certainly reprehensible. Owing to the acid in, or developed in, the cheese the foil becomes crumbly, and even when the cheese is first covered with greased paper, particles of the oxidized foil are very likely to become attached to the cheese as it is used. Attention has been repeatedly called to this matter abroad, among others by Wittstein (Dingl. pol. Journ. **208**, 341,) who found appreciable amounts of lead in cheese thus wrapped.

TABLE VI.

No.	Amount taken		Amount found in grams.		Percentage.	
	Size in sq. in.	Weight in grams.	Tin.	Lead.	Tin.	Lead.
21	6	0.2650	0.2653	...	100.10	...
22	6	0.5145	0.5130	...	99.70	...
23	6	0.2560	0.2559	...	99.96	...
24	6	1.1175	0.1111	1.0040	9.94	89.87
25	...	1.1600	0.2570	0.8733	22.15	75.27
26	...	0.7915	0.1645	0.5793	20.77	73.19
27	6	0.4435	0.4419	...	99.63	...
28	2	0.4850	0.0938	0.3879	19.34	79.99

MASS. INST. OF TECHNOLOGY, BOSTON, MASS.

REDUCTION OF NITRATES BY FERMENTS.

BY ALFRED SPRINGER.

A year and a half ago, while experimenting with infusions of the roots of plants in water, I noticed a copious evolution of nitric oxide proceed from those rich in nitrates. It immediately struck me that this arose from the action of small organisms which covered the roots of plants. Starting out with this idea, I made separate infusions of the roots, stems and leaves of tobacco, and divided each set into four parts. Fermentation was excited in the first by the addition of small quantities of yeast, in the second by urine, in the third by the so-called spontaneous method, and in the last by the newly discovered ferment. Not only were the nitrates originally present completely dissociated, but also considerable quantities of freshly added nitrates underwent the same process. All the infusions contained amongst other ferments one special kind, noticeable by its extreme activity. In appearance it closely resembles the butyric ferment, being composed of small cylindrical rods rounded at the extremities, generally isolated, or, when joined, two by two acting as one body. They move rapidly with a wriggling motion and often bend their bodies until they form a perfect circle. Another ferment or modification of the former is present which is

somewhat smaller and spins around its smaller diameter as an axis. Phenol has no appreciable effect on the new ferment, and gave the means of partly isolating it from others.

Believing that to this ferment is owing the power of dissociating the nitrates of the soil, I have begun a series of experiments to decide the question.

I give these preliminary statements in regard to my work on account of the experiments lately made in France by Gayon and Dupetit[1] and Deherain and Marquenne,[2] the results of which closely agree with mine as stated at the Ohio Mechanic's Institute a year ago. I also, like the above-mentioned chemists, obtained quantities of butyric acid. There is little doubt but that the ferment mentioned by Béchamp[3] when working with chalk from cretaceous formations instead of pure precipitated calcium carbonate, and by him called *Microzyma cretae*, is the same as the one obtained by me from plant infusions. Perhaps the conflicting descriptions of butyric ferments are often owing to the presence of this widely-spread ferment; which may be either a modification of the butyric ferment caused by abnormal influences bearing upon it, or an entirely different one.

Although it may be classed among the anaerobics, air does not kill it, nor stun it for any length of time. For its greatest activity, temperatures lying between 35° and 40° C., and much water, are most propitious. The great amount of these ferments upon the roots of plants, less on the stems, and least on the leaves, leads me to believe that their presence is some sort of a link between the plants and their nitrogenous constituents. In order to test this hypothesis I have now in my laboratory soil first heated to 120° C., whereby the ferments are killed; this is placed in bottles supplied with air filtered through cotton. In some of the bottles well washed seeds and roots are sown; in some cases the ferments are added, and in others their presence is avoided.

CINCINNATI, *Jan.* 11, 1883.

[1] Comptes rendus **95**, 644-46. [2] *Ibid.* **95**, 691-93. [3] Bull. Société chimique [2] **6**, 484.

ON THE CONDUCT OF MOIST PHOSPHORUS AND AIR TOWARDS CARBON MONOXIDE.

By Ira Remsen and E. H. Keiser.

Recent experiments have drawn attention anew to the question concerning the existence of an active form of oxygen distinct from ozone, and capable of effecting changes which ozone cannot effect. Hoppe-Seyler[1] and Baumann[2] hold that the oxidizing action of palladium-hydrogen is due in the first instance to the splitting up of the molecule of ordinary oxygen by the active hydrogen, resulting in a momentary liberation of atoms of oxygen which exhibit very active properties. Traube,[3] on the other hand, holds that this action is due to the formation of hydrogen dioxide, and that the oxidizing effects noticed are only those of the dioxide. At first, however, this explanation did not appear probable, for Baumann had shown that palladium-hydrogen in the presence of oxygen has the power of oxidizing carbon monoxide, and one of us[4] had previously shown that hydrogen dioxide has not this power. Traube afterwards conceded this point, but then showed that, while hydrogen dioxide itself has not the power of oxidizing carbon monoxide, it has this power in the presence of palladium. We have repeated the experiment of Traube, and can confirm his statement.[5] From the evidence thus far submitted, Traube's explanation of the oxidizing action of palladium-hydrogen certainly appears to be more probable than that of Hoppe-Seyler.

There is, however, one experiment recorded which indirectly lends some support to Hoppe-Seyler's explanation. We refer to the experiment first performed by Leeds,[6] and subsequently by Baumann,[7] which consisted in bringing air and carbon monoxide together in the presence of moist phosphorus. Under these circumstances, according to both authors, oxidation of the monoxide

[1] Hoppe-Seyler, Zeitschrift für physiologische Chemie, **1**, 396; **2**, 22, 25.

[2] Baumann, *Ibid.* **5**, 244.

[3] Traube, Berichte der deutschen chemischen Gesellschaft, **15**, 659; 2421; 2434; 2854.

[4] Remsen, This Journal, **4**, 50.

[5] We noticed that if a small quantity of free hydrochloric or sulphuric acid is present in the hydrogen dioxide, some of the palladium is dissolved. Similar observations have been made by Fairly (Berichte der deutschen chemischen Gesellschaft, **8**, 1600; **9**, 948), though the statements which we have seen concerning this phenomenon are very meagre.

[6] Journal American Chemical Society, **1**, 232.

[7] Zeitschrift für physiologische Chemie, **5**, 250.

is effected. Accepting the conclusion, the simplest interpretation of the fact is this: The phosphorus acts upon the oxygen, splitting the molecules, uniting with some of the free atoms and momentarily setting others free. The free atoms then unite with oxygen molecules to form ozone, and with carbon monoxide to form the dioxide. This view is similar to that first put forth by Hoppe-Seyler to account for the oxidizing action of palladium-hydrogen as above related. If, then, the result reached by Leeds and by Baumann is correct, we have some evidence, though it is not conclusive, of the existence under some conditions of a form of oxygen more active than ozone. We say it is not conclusive, for, as hydrogen dioxide is formed under these circumstances, we may assume that the action is due to combined influence of the dioxide and phosphorus.

The importance of the subject has led us to repeat the experiments of Leeds and of Baumann, and we have been led to a conclusion directly opposed to that recorded by these authors. As they apparently worked with great care and both agree, it will be necessary for us to describe our work in detail in order that any who may wish to convince themselves may avoid sources of error which have been overlooked in the earlier experiments.

We tried first the effect of passing air alone, freed from carbon dioxide, over moist phosphorus. After its exit from the vessel containing the phosphorus it was filtered through a layer of previously ignited asbestos contained in a tube between two and three feet long, and then into a vessel containing clear baryta water. A precipitate was formed at once, and increased in quantity the longer the current continued. It was tested for phosphoric acid and for phosphorus compounds in general, but not a trace of these could be detected. The passage of air through the apparatus was continued for some days for the purpose of collecting enough of the precipitate for examination and analysis. It proved to be nothing but barium carbonate.

The carbon dioxide must have come from one of two sources, either from some carbonaceous material contained in our phosphorus, or as the result of the action of ozone on the cork stoppers used to make connections. The exposure of rubber had been avoided almost entirely, but still there was some slight opportunity for contact of the ozone with the rubber in consequence of diffusion. As, however, we had here taken the same precautions as in the earlier experiments on carbon monoxide and ozone; as, fur-

ther, Baumann[1] appears to have experienced no difficulty from the use of rubber joints, it seemed not improbable that the trouble in our experiment was in the chemical condition of the phosphorus. We hence procured specimens of phosphorus from as many different sources as possible, and with each of these repeated the above described experiment, using the same form of apparatus. In every case the precipitate of barium carbonate was obtained, and, as far as could be estimated, in about the same quantity. Attempts were then made to purify the phosphorus. One specimen was placed in hot water under the receiver of an air-pump, and the air exhausted for the purpose of getting rid of any gases which might be contained in the phosphorus. Other specimens were distilled in an atmosphere of pure hydrogen and the vapor condensed in cold water.[2] No matter what process of purification was adopted, the phosphorus acted in the same way after the purification as before.

Attention was now directed specially to the corks and rubber connections. An apparatus was finally constructed in which these were entirely excluded, or, at least, so protected that the ozone could not possibly reach them. Although a number of different forms of apparatus were tried, we need only describe that which we finally decided upon as the best. This consisted of a flask of from three to four litres capacity, provided with a doubly perforated cork stopper. Through this there passed one glass tube reaching to the bottom of the flask, and another reaching only half-way. Outside the flask the shorter tube was connected with the apparatus intended to remove the carbon dioxide from the air, and the longer tube was bent twice at right angles, and then passed through the stopper of a U-tube about eight inches high. Between this U-tube and a second like it, connection was made by means of a doubly bent glass tube. In the flask there were placed usually two or three sticks of phosphorus each three or four inches long, and enough pure water to somewhat more than fill the neck when the flask was inverted. The U-tubes were filled with ignited asbestos, and there was then added some mercury so that when the tubes were inverted, in which position the entire apparatus was placed when in use, the metal covered the corks with a layer from

[1] *Loc. cit.*

[2] In this way a new modification of phosphorus, "white phosphorus," was discovered. See next paper.

three-quarters of an inch to an inch in thickness. The connecting tubes passed, of course, in each case through the layer of mercury. The vessel containing the clear baryta water was also connected with the last U-tube by means of a mercury joint similar to those above described. The baryta water was protected from the action of the air by placing before it a small U-tube containing potassium hydroxide, and this last tube was connected with an aspirator. Before connecting the bulbs containing the baryta water, air freed from carbon dioxide was drawn slowly[1] through the apparatus. On now connecting with the baryta-water bulbs no precipitate was formed. Even on allowing the air to remain in contact with the moist phosphorus for periods varying from one to twelve hours, no carbon dioxide could be detected. This experiment was tried over and over again at different temperatures, but always with the same result.

About one-third of the air in the ozone flask was now replaced by carbon monoxide from which all dioxide had been scrupulously removed. The mixture was allowed to stand for some hours and then drawn through the baryta-water bulbs, when no precipitate was formed. This experiment was repeated a number of times with the same result. In some cases the air and carbon monoxide were drawn together slowly for a long time over the moist phosphorus, but this made no difference in the result. So frequently was the experiment performed, so great were the precautions against error, and so undeniably negative were the results, that, in spite of the explicit statements of Leeds and of Baumann, we do not hesitate to say that carbon monoxide is not oxidized when exposed to the action of air and moist phosphorus. It follows, of course, from this that the action of air and moist phosphorus on carbon monoxide furnishes no evidence in favor of the view that there is an active condition of oxygen distinct from ozone.

Leeds's error is easily explained. In the first place he took no special precautions to protect the corks from the action of the ozone, and in the second place he passed the gases through a filter of moist cotton for the purpose of removing "oxides of phosphorus." Now cotton, as it is usually met with, yields carbon dioxide when subjected to the influence of ozone, so that the carbon dioxide noticed by Leeds was probably the result of the action of ozone on

[1] This operation requires care and constant attention. The phosphorus not unfrequently takes fire. In one case in our experience it took fire after having stood quietly and unmolested for several hours.

the cotton or the oily substances which always adhere to it. To test the probability of this explanation, we introduced a short plug of cotton into one of the tubes of our apparatus. It having been shown previously that the air drawn through this apparatus contained no carbon dioxide, it was now found that the presence of the cotton alone soon caused the appearance of a precipitate in the baryta water. This experiment was frequently repeated.

Baumann describes his experiments thus:[1] "Ein langsamer Strom von kohlensäurefreier Luft wurde durch eine Flasche in welcher sich feuchter Phosphor befindet, und von da in eine zweite Flasche übergeleitet, in welcher die ozonosirte Luft einem etwas langsameren Strom eines kohlensäurefreien Gemenges von 3 Volum Sauerstoff und 1 Volum Kohlenoxyd begegnet; aus dieser Flasche treten die Gase durch klares Barytwasser. Das Barytwasser blieb, nachdem aus dem Apparate selbst erst alle Kohlensäure entfernt war, bei 6-stündigem Durchleiten der Gase völlig klar. Wurde dagegen die Mischung von Kohlenoxyd und Sauerstoff in die Flaschen eingeleitet, in welcher der Phosphor sich befand, und nach unserer Vorstellung aktiver Sauerstoff auftreten muss, so ist das Resultat ein ganz anderes: das vorgelegte Barytwasser wird schon nach kurzer Zeit trübe und im Laufe einer Stunde bildet sich ein reichlicher Niederschlag von kohlensaurem Baryt."

Nothing is said about stoppers or rubber connections, and it is safe to assume that, in the apparatus used by Baumann, ozone came in contact at some points with organic matter. Hence the formation of carbon dioxide is easily accounted for. But to account for the negative result when no carbon monoxide was used is not so easy. It can only be said that, if the ozone formed is not concentrated, the action on organic connections is not marked. Now, if the temperature should happen to be a few degrees lower than the ordinary temperature of rooms, the formation of ozone would be retarded and there might not be formed enough to act perceptibly on the stoppers, &c. The rate of the current of gas is also of importance. The more rapid the current of air passed over the phosphorus the less ozone it contains, and indeed unless the current be quite slow the oxidizing effect of the ozone on the organic connections does not reveal itself by the formation of a precipitate in the baryta water. Whatever the sources of error in Baumann's experiment may have been, we are confident that a repetition with the precautions taken by us will show him that his conclusion is wrong.

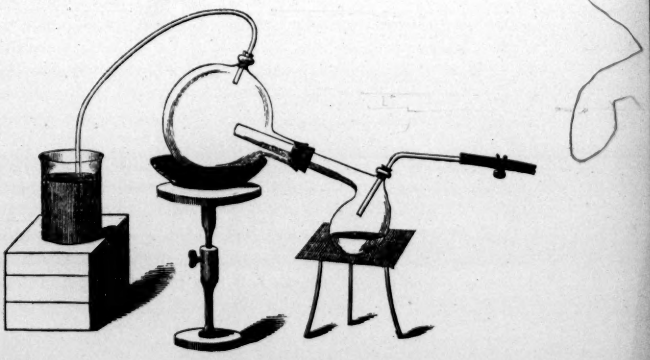
[1] Zeitschrift für physiologische Chemie, 5, 250.

WHITE PHOSPHORUS.

By Ira Remsen and E. H. Keiser.

In the course of the experiments described in the preceding paper, the suspicion arose that the phosphorus with which we were working might contain some carbonaceous impurity. With the view of removing this if possible, we distilled some of the phosphorus in an atmosphere of purified hydrogen and condensed the vapor on cold water. We were much astonished to find that the substance thus obtained differed very markedly in appearance from ordinary phosphorus, and indeed we thought at first that it could not be the element, but must probably be some new oxide, formed in consequence of a slight leak in the distilling apparatus. It floated on the surface of the water in the receiver, forming a snow white layer about a quarter of an inch in thickness. On examining it more carefully it was found that it was insoluble in water, and could be changed to ordinary phosphorus very easily. The entire quantity obtained in the first experiment happened to be brought into some warm water and was changed at once to ordinary phosphorus. We now endeavored to prepare the substance again, but found considerable difficulty in meeting the right conditions. While we always obtained some of it, we were obliged to make a large number of experiments before the conditions of success became clear. The experiment should be performed as described in detail below.

An apparatus like that roughly illustrated in the accompanying figure should be used.



It is essential that the neck of the retort be inclined upward and that it project well within the receiver. In the receiver there is a layer of ice-cold water from one to one and a half inches deep in the deepest part. In this, lumps of ice are brought, enough to form a fairly compact mass of ice. The receiver rests in a vessel containing cold water. The beaker into which the bent tube dips also contains cold water. Two or three sticks of ordinary phosphorus having been brought into the retort, connection is made by means of the rubber tube with a hydrogen-generating apparatus. The hydrogen is passed first through a solution of potassium permanganate and then through the apparatus as above sketched. As soon as the apparatus is completely filled with the gas the current of hydrogen is stopped by means of the pinch-cock. The distillation is now begun. As soon as the phosphorus vapor reaches the end of the neck of the retort it falls down on the ice and water and forms a white coating. Under some circumstances the material is deposited in piles reaching the height of half an inch to an inch. The principal precaution necessary is to prevent the boiling from becoming so active that the vapor condenses to form liquid just after it leaves the retort neck. In successful operations there will be found at the end a cake of white material floating on the surface of the water, varying in thickness according to the amount of phosphorus distilled. Usually this is quite thin. In order to remove it, it is best to allow the whole apparatus to cool down to the temperature of the air, then to disconnect the retort from the receiver, and put the receiver, with its contents, under water in a larger vessel. In this way the hydrogen can be displaced without danger, and afterwards the white phosphorus can be easily removed. If the above precaution is not taken the receiver becomes filled with a mixture of hydrogen and oxygen while the phosphorus is being taken out, and a little friction may set fire to the phosphorus, thus giving rise to an extremely unpleasant explosion. This actually happened in one of our experiments, and one of us (K.) still carries the marks of the explosion.

White phosphorus is light and plastic. If placed on a piece of bibulous paper so that the water is absorbed from it, it gives off dense white fumes, melts but does not take fire, and is then nothing but ordinary phosphorus. It dissolves readily in carbon bisulphide. It melts at exactly the same point as ordinary phosphorus, and at this point is completely transformed into the latter. From these

statements it seems clear that this curious substance bears to ordinary phosphorus much the same relation as "flowers of sulphur" to "roll brimstone." It is in a different physical condition. It is much less susceptible to the influence of sunlight than ordinary phosphorus. We have in our possession some specimens made last October which have undergone very little change, though they have not been specially protected from the action of the light. One specimen, which was purposely placed where the direct sunlight would be upon it for some time every day, has become slightly yellow, but is otherwise, as far as we can judge, quite unchanged. It is still plastic, and when dried acts as above described.

We have not been able to find any references in chemical literature to a substance like that which we have described. The white phosphorus referred to in the communications of Pelouze,[1] H. Rose,[2] Caignard-Latour,[3] Mulder,[4] Marchand[5] and Baudrimont[6] is the coating found on sticks of ordinary phosphorus which have been preserved under water. Böttger[7] also speaks of a variety of white phosphorus prepared by dissolving ordinary yellow phosphorus in alcoholic potassium hydroxide, pouring off the liquid after the phosphorus has become perfectly clear and then adding ice-water. The phosphorus solidifies as a snow-white brittle mass, which can be pulverized under water. From Böttger's description of his product it is evident that it must be quite different from our white phosphorus.

REVIEWS AND REPORTS.

Report on Progress in Physiological Chemistry.

[*Continued from Vol.* 4, 218.]

Gastric Digestion.

Digestion of Elastic Tissue.—Among the many bodies allied to albumin, elastin, the organic basis of elastic tissue, has long been considered as but partially or with difficulty digestible in gastric

[1] Annales de Chimie et de Physique, **50**, 83.
[2] Poggendorff's Annalen, **27**, 563.
[3] L'Institut, 1834, No. 34.
[4] Journal Pharmacie, **23**, 20.
[5] Journal für praktische Chemie, **20**, 506.
[6] Comptes rendus, **61**, 857.
[7] Journal für Chemie und Physik, **67**, 141, and **68**, 141.

juice. Recently Horbaczewski[1] has investigated the subject anew, with quite interesting results. Elastin prepared from the *ligamentum nuchae* of the ox by the usual methods of successive extraction with water, alkali, acid, alcohol and ether, was obtained absolutely free from sulphur, and with the following composition:

C 54.32, H 6.99, N 16.75.

The finely powdered elastin was readily dissolved and digested by .1 per cent. as also by .2 per cent. hydrochloric acid gastric juice, while in acid of the same strength it remained an equal length of time unaffected. Under the microscope the small fibres were seen to swell up during the first stage of digestion, and to become transparent, similar to shreds of fibrin under like conditions. The old view of the non-digestibility of elastin is undoubtedly dependent on the slowness with which it is dissolved when compared with albumin, and Horbaczewski has found that the rapidity of its digestion stands directly related to the fineness with which it is broken up. .3 gram of finely powdered elastin is completely dissolved in 24–72 hours in 50 cc. of active gastric juice at 40° C.

In order to study the products of digestion, 100 grams of the elastin powder were digested with 1500 cc. of .2 per cent. hydrochloric acid and 1.5 gram of Brücke's pepsin,[2] until the elastin was wholly dissolved. The fluid was then dialyzed until all acid was removed, filtered and evaporated to dryness. A yellowish, gummy powder was obtained, which on further examination showed itself to be composed of two bodies, easily separated from each other. The one was precipitated from its aqueous solution by acetic acid and potassium ferrocyanide or by hydrated lead oxide, and is evidently analogous to the hemialbumose of Kühne and Salkowski. This body Horbaczewski calls hemielastin. Precipitated from its solution by acetic acid and salt and then dialyzed, it shows when dried at 110° C. the following composition:

C 54.22, H 7.02, N 16.84,

by which it is seen that it does not differ from the original elastin. It is readily soluble in cold water, but wholly insoluble in hot, and a very dilute cold water solution is coagulated by long boiling. The hemielastin gives the biuret reaction similar to albumin, likewise the xanthoprotein, only less intense. Hemielastin dried at 100–120° C. loses many of its properties, becoming insoluble in water, shows a marked resistance to the various solvents, similar to elastin, and indeed does not differ in any of its chemical reactions from elastin proper. This makes the third product of digestion which by dehydration can be reconverted into the mother substance. Being amorphous and devoid of the structural elements of the original elastin, it is called *structureless* elastin.

[1] Zeitschrift f. physiolog. Chem. **6**, 330. [2] Pflüger's Archiv. **9**, 585.

The second product of the digestion of elastin, the elastin-peptone when freed from hemielastin by carbonate of lead, has the following composition:

C 53.57, H 8.07, N 16.20.

The aqueous solution does not differ in any respect from a solution of albumin peptones, and indeed it would be hardly possible to separate the two. It is thus apparent that elastin, particularly through its digestion products, stands closely related to albumin; the two intermediate products of digestion, hemielastin and hemialbumose, being closely analogous bodies in nearly all of their reactions, while the two end products, the peptones, are equally related. Whether elastin as a constituent of flesh has any importance as nourishment is perhaps questionable. When sufficiently finely divided it is certainly soluble and digestible, and in this condition it is without doubt absorbable. In this connection it may be mentioned that Horbaczewski had an opportunity of studying the digestibility of elastin in the human stomach. 1 gram of elastin powder placed in a small bag of very fine muslin was introduced into the stomach of a hospital patient with an artificial gastric fistula, whose digestion was otherwise normal. After 24 hours it was found that two-thirds of the elastin had disappeared, while a thick swollen mass still remained, which, on treatment with water, yielded a solution giving a strong reaction for hemielastin. Thus here, under not very favorable circumstances, since the powder was swollen to a thick lump, the elastin was digested with a moderate degree of rapidity.

Years ago Schultze[1] observed that when elastin was heated for 30 hours with water at 100° C. in a Papins digestor it was dissolved. The resulting body has ever since been generally considered as pure gelatin from the elastic fibres. Horbaczewski has repeated the experiment by heating 2 grams of powdered elastin with 50 cc. of water in a sealed glass tube for 20 hours at about 100° C. The solution he found to contain a body having all the properties of elastin-peptone, the formation of which we should from analogy naturally expect.

Digestion of Milk in the Stomach.—Uffelman[2] has subjected milk to a careful study in reference to the changes which it undergoes during digestion. He finds that when cow's milk is mixed with .2 per cent. hydrochloric acid in certain proportions, dependent in part upon the amount of water and salts in the milk, a fine granular precipitate is obtained, instead of the ordinary coagulum; thus if 10 cc. of .2 per cent. hydrochloric acid are placed in a cylinder and fresh milk added in quantities of ½ cc., it will be found that when about 7.5 cc. have been added, a fine dust-like precipi-

[1] Annalen der Chem. u. Pharm. **71**.
[2] Studien über die Verdauung der Kuhmilch und über die Mittel, ihre Verdaulichkeit zu erhöhen, Pflüger's Archiv. **29**, 339.

tate begins to appear, which however is quickly changed into a flocculent one if a few drops more milk are added, or quickly dissolved if a few cubic centimetres of the dilute acid are added. Again, if cow's milk is mixed with .2 per cent. acid in such proportion that the coagulum at first formed is dissolved, viz. 25 cc. fresh milk and 35 cc. .2 per cent. acid, it will be found that even on long standing in an open dish at a temperature of 18–19° C. no change will be noticed other than the formation of a layer of cream. Evidently the proteid matter of the milk in the presence of the acid and possible ferments undergoes a chemical change, although not perceptible to the eye. In fact Uffelman has found by repeated experiment that a mixture of acid and milk in the above proportion standing at the ordinary temperature of a room for 24 hours, yields on an average about .3 gram of peptones. The milk employed in the experiments contained 4.78 per cent. of proteid matter, of which therefore 20–25 per cent. is under these conditions changed into peptones. As is well known milk usually contains a trace of peptones. Pfeiffer[1] however has quite recently found a constant and appreciable "albumin-residue" in the analyses of both human milk and cow's milk which has all the properties of peptones. Precipitated by solution of tannin, it amounts on an average in human milk to nearly .5 per cent., while in cow's milk it is present to the extent of .73 per cent. in milk containing 2.33 per cent. casein and .22 per cent. albumin.

In the artificial digestion of milk with acid and pepsin, Uffelman finds that the rapidity and thoroughness of digestion are greatly influenced by the relative proportion of acid and milk, being dependent on the presence or absence of the thick, cheesy clots of casein; thus in a 4 hours' digestion 25 cc. of milk mixed with 33.5 cc. of a .2 per cent. acid gastric juice yielded peptones corresponding to 81 per cent. of the proteid matter present, while the same quantity of milk mixed with 7.5 cc. of the same gastric juice yielded only 50 per cent. The digestive action is somewhat retarded by the presence of an excess of lactic acid. In regard to the absorption of milk or the products of its digestion, Uffelman has found by experiments on himself and young infants the following results:

Percentage amounts absorbed in a purely milk diet.

	4 weeks old boy.	5¾ months old boy.	11¼ months old boy.	Uffelman
Albumin,	99.20	99.40	98.50	98.70
Fat,	92.20	94.90	93.30	93.40
Salts,	45.40	51.00	57.00	44.20
Sugar,	100.00	100.00	100.00	100.00

As an average of results from four infants, 92.50 per cent. of the milk was absorbed, while in Uffelman's own case only 90.5 per cent. was absorbed. It is thus evident that either from an excess of acid or other cause, a young infant possesses the power of digest-

[1] Zeitschrift für analytische Chemie, **22**, 19, 1882.

ing and absorbing milk better than an adult. These results are in close accord with those of Rübner and Gerber.[1]

Metabolism.

In 1875 Pflüger[2] advanced the theory that living protoplasm differs in its chemical constitution from dead protoplasm. The albumin molecule, so soon as it becomes a constituent of a cell, as in the brain or muscle, "loses its indifference and begins to breathe, to live." An old and favorite theory for explaining the manner in which food albumin is changed into the cell substance was based upon a possible loose union of the hydroxyl group in the albumin molecule, a general principle according to which many of the known synthetical changes in the body are produced, in a manner analogous to the formation of hippuric acid and other bodies. Pflüger favored the belief that the formation of albumin in the tissues depends upon an ether-like combination of molecules, as in the union of the various parts of the lecithin molecule. Thus albumin passing from the state of dead protoplasm to living, might naturally be expected to show a constitutional difference, and *vice versa*. Pflüger sought for an explanation of the changes which living protoplasm undergoes by a study of the products of animal oxidation, and he was led to the belief that the non-nitrogenous oxidation products obtained outside the body did not differ essentially from those produced in the organism. From which it would follow that living albumin, so far as its hydrocarbon radicals are concerned, does not differ materially from food albumin. But the nitrogen products in the artificial decomposition of proteid matter are quite different. Thus the decomposition products, urea, uric acid and others of regressive metamorphism, notably creatin, guanin, etc., are never obtained artificially from albumin. These latter bodies contain the cyanogen radical, and Pflüger argues that living albumin contains the greater part of its nitrogen in the form of CN and not NH_3, none of the decomposition products containing the former group having ever been obtained from dead albumin. Thus in the formation of living protoplasm from food albumin a change is effected in which the nitrogen atoms pass into the cyanogen compounds, and, on the death of the protoplasm, again return to the more stable condition of amides. Hence, according to the views of Pflüger, the ready decomposition of living protoplasm is to be sought for in the presence of the cyanogen group. Quite recently Loew and Bokorny in a series of interesting papers[3] have advanced the idea of a different structure

[1] Zeitschrift für Biologie, 1880, 16.

[2] Ueber die physiologische Verbrennung in den lebendigen Organismen, Pflüger's Archiv. **10**, 251. Also abstract in Jahresbericht der Thierchemie, **5**, 238.

[3] Eine Hypothese über die Bildung des Albumins, Pflüger's Archiv. **22**, 503, 1880. Eine chemischer Unterschied zwischen lebendigen und todten Protoplasma, Pflüger's Archiv. **25**, 150, 1881. Ueber das absterben pflanzlichen Plasmas unter verschiedenen Bedingungen, Pflüger's Archiv. **26**, 50, 1881. Einige Bemerkungen über Protoplasma, Pflüger's Archiv. **28**, 94, 1882. Ueber die Aldehydnatur des lebenden Protoplasmas, Ber. d. deutsch. chem. Gesell. **14**, 2508. Die chemische Ursache des Lebens, Munich, 1881. Die chemische Kraftquelle im lebenden Protoplasma, Munich, 1882.

of the albumin molecule, and like Pflüger have attempted to establish a chemical difference between living and dead protoplasm. These investigators consider "albumin like sugar as a condensation product of bodies of a comparatively simple constitution." Loew's view is that the CHOH group, an isomer of formaldehyde or methyleneoxide, serves as the material for building up the albumin molecule; the aldehyde group itself being possibly formed from various allied substances, such as acetic and tartaric acids, by "*pilz*" growth. For the detection of the aldehyde groups in living albumin Loew and Bokorny experimented mostly with needle-like algae, particularly the various species of Spirogyra and Zygnema, although like results were obtained with other algae such as Vaucheria and Cladophora. Sections from Salix and Syringa also gave satisfactory results, likewise leaves from Valisneria. While various reducing solutions were employed in the reactions, most of the results were obtained with an ammoniacal solution of silver nitrate mixed with potassa and containing 1 part of $AgNO_3$ in 100,000 parts, from which living cells separate the silver while the dead ones do not. The reducing action of the living protoplasm is best shown by placing portions of the cellular algae in a large quantity of the reagent and allowing them to remain there for several hours; if heated to 30° C. the action takes place much quicker. Under the microscope the plasma of the needles is seen to be quite black from reduced silver, while the single cells show numerous black dots or large lumps of silver. The reduction is particularly noticeable in those parts of the protoplasm where the greatest activity would be expected, as in the chlorophyll granules and at the ends of the cylindrical tubules. This reduction of silver is what Loew and Bokorny call the "reaction of life," and really constitutes the only evidence of the existence of aldehyde groups in living protoplasm. In dead cells, however, such reducing action cannot be obtained. Thus in the case of the cellular algae, death of the protoplasm was induced by all possible methods, such as starving, drying, exposure to high temperatures, electrical shocks, mechanical pressure, poisons, anaesthetics, etc., and in nearly every case these methods were sufficient to prevent the reducing action: thus a thread of Spirogyra heated at 50° C. for five minutes or dried between blotting-paper and then exposed to ether vapor for an hour, completely lost the power of reduction. Quinine solutions, however, although they completely disintegrate protoplasm, do not prevent the reducing action from taking place. That the various methods used in the killing of the protoplasm do not remove any possible reducing substances present in the tissue, is plainly apparent from the fact that cells killed by simple pressure lose their power of reducing the silver solution as completely as by more certain means of death, although it must be confessed that it is difficult to understand how the aldehyde group can be broken up by simple pressure, if that is to be inferred. Having thus established the existence of a chemical difference between living and

dead protoplasm, Loew advances next to the probable constitution of the albumin molecule. Starting with the idea that an isomer of formaldehyde is the probable antecedent, he considers three successive stages necessary for the construction of the completed molecule. In the first, four aldehyde groups are necessary together with one molecule of ammonia, by the combination of which a body can be formed in which the numerical proportion of carbon to nitrogen would be as 4 : 1, and which would therefore by condensation be able to furnish the albumin molecule,

$$4HCOH + NH_3 = H_2N.CH.COH \\ \quad\quad\quad\

It is undoubtedly true that Loew's somewhat fanciful arrangement of the atoms in the complex albumin molecule coincides with the fact that asparagin is one of the principal products of proteid decomposition in plant life, and moreover the formation of asparagin would thereby be readily explainable. Again, Schultze's statement that much more asparagin is formed in nature than is found in the decomposition of albumin by acids, would favor the idea that the decomposition of albumin in the cells is a process of quite a different character. In a like manner the proposed constitutional formula would account for the formation of the saccharine groups found by Schützenberger[1] in the decomposition of albumin, and also the peculiar formation of glycogen in the animal body after a purely albuminous diet. While these latter views are wholly theoretical in their nature, and perhaps hardly worthy of credence in their entirety, there is at least a grain of wisdom in them, and surely nothing which promises to throw any light upon the complex metabolism of protoplasmic matter is to be cast aside without careful scrutiny. It is only to be regretted that there are not more facts at our disposal to sustain Loew's ingenious theories. Since Loew and Bokorny's first papers were published, Reinke[2] has given an account of the presence in chlorophyll plant cells of an aldehyde-like body of great volatility and energetic reducing power both towards alkaline silver and copper solutions. Reinke considers this body to be formaldehyde, which, according to A. Baeyer's view, is the first assimilation product formed in green plants. By distillation of the neutralized juices from plants containing chlorophyll, Reinke obtained in the first few cubic centimetres of the distillate the above-mentioned reducing substance, while plants free from chlorophyll failed to yield any, from which Reinke inclines to the view that this body is the source, in part at least, of Loew and Bokorny's aldehyde reactions in living protoplasm.[3]

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(To be continued.)

ANALYTICAL CHEMISTRY.

Antimony.—"Volumetric Estimation of Antimony in presence of Tin." By E. F. Herroun.[4] The process which is applicable to alloys such as Britannia or type metal, depends upon the fact that antimonic chloride is reduced to antimonious chloride by hydriodic acid with liberation of iodine, while stannic chloride is not reduced. The alloy, in a state of fine division, is dissolved in strong hydrochloric acid with the aid of heat and with frequent additions

[1] This Journal, **2**, 209. [2] Bericht. d. deutsch. chem. Gesell. **14**, 2144.
[3] In Pflüger's Archiv. **29**, 400, 1882, Bauman, of Berlin, criticises Loew and Bokorny's views, purely, however, on theoretical grounds. [4] Chemical News, **45**, 101.

of small quantities of potassium chlorate. After the metal is entirely dissolved a piece of potassium chlorate is added to insure the conversion of the antimonious chloride into antimonic chloride, and the solution gently boiled until all the oxides of chlorine have been expelled. The solution is then allowed to cool, and a slight excess of a strong solution of potassium iodide added. The free iodine is then estimated by means of a standard solution of sodium hyposulphite.

If iron, or any other metal whose perchloride is capable of liberating iodine, be present in the alloy, the tin and antimony may be separated by conversion into their oxides by treating the alloy with nitric acid.

A. Weller [1] has made use of the same principle in determining antimony. But his process differs from that of Herroun in the manner of determining the amount of liberated iodine. In Weller's process the iodine is distilled off from the antimonious chloride, collected in potassium iodide and estimated volumetrically by means of sulphurous acid and a standard iodine solution. A number of analyses are given in support of the method. Weller claims priority for the discovery, because his work was done in 1879 and 1880.

Bismuth.—"Volumetric Estimation of Bismuth in the form of Oxalate." By Pattison Muir and C. E. Robbs. The authors described a method [2] for estimating bismuth by precipitation as neutral oxalate, and conversion into the acid oxalate, by washing with boiling water. This process involves boiling the precipitated oxalate for some little time with successive quantities of water, collection and complete washing of the acid oxalate, and its solution in acid, before titration with potassium permanganate. They now propose to make use of the double salt of potassium and bismuth, obtained by adding normal potassium oxalate to a solution of bismuth containing acetic acid and nearly free from mineral acid, and which has the formula $Bi_2(C_2O_4)_3.K_2C_2O_4$ according to Reis.[3] The solution of bismuth is evaporated nearly to dryness, dissolved in nitric acid, evaporated nearly to dryness again, then an excess of glacial acetic acid added, and the whole transferred to a measuring flask. About twice as much potassium oxalate as bismuthous oxide is added, and the flask filled to the mark with acetic acid (1 : 1). The liquid is shaken and allowed to stand for some time, then filtered through a dry filter, and the residual oxalate determined by titration with permanganate. When a large excess of potassium oxalate is used the results are invariably too low, unless a large quantity of glacial acetic acid is added; the double oxalate being soluble in an excess of potassism oxalate, but is reprecipitated by addition of much strong acetic acid. It is best to run in the potassium oxalate from a standard solution in a burette in small successive quantities;

[1] Liebig's Annalen der Chemie, **213**, 365. [2] Journal of the Chemical Society, 1878, p. 70.
[3] Berichte der deutschen chemischen Gesellschaft, **14**, 1172.

when the precipitation is apparently complete a few cubic centimetres more are added.

In applying this process to the determination of bismuth in mixtures, it is necessary that the bismuth should be separated from other heavy metals; this may be done by precipitation as oxychloride. The bismuth also should be obtained as nitrate with a small excess of nitric acid.

Zinc.—M. Schroeder[1] recommends the use of thallium instead of lead or cobalt paper in the volumetric determination of zinc by means of sodium sulphide. It is more sensitive than cobalt paper, and is to be preferred to lead paper because it is not affected by zinc sulphide, provided the amount of free ammonia present is extremely small. The amount of ammonium chloride present is of little significance in the use of this indicator.

Cadmium.—Anton Orlowski[2] recommends two different methods for the detection of cadmium in the presence of copper.

First method: After the separation of bismuth hydroxide by means of ammonia, the blue solution is acidified with hydrochloric acid and treated with stannous chloride until the color disappears; milk of sulphur is then added and the liquid heated to boiling. By this means all of the copper is precipitated as black cuprous sulphide. The precipitate is separated by filtration and an excess of ammonia added, which precipitates the tin as stannous hydroxide while the cadmium remains in solution. A yellow precipitate produced by ammonium sulphide in the filtrate indicates the presence of cadmium.

Second method: This is the same as that proposed by G. Vortmann[3] in which copper is precipitated as sulphide by means of hyposulphite of sodium. Orlowski remarks that he had not seen the article of Vortmann until his own was ready for publication.

Silver.—Jean Krutwig[4] finds that traces of silver in lead ores may be quantitatively as well as qualitatively determined in the following manner: 20 to 25 grams of the lead ore are decomposed in an iron crucible with borax, soda and cream of tartar. The lead thus obtained, which contains besides iron and sulphur all of the silver, is dissolved in concentrated nitric acid, water added and the lead sulphate filtered off. The filtrate is then treated with an excess of caustic soda and allowed to stand for some time. The brownish yellow precipitate containing iron; lead and silver is filtered. This precipitate, which consists of lead and iron hydroxide and a so-called plumbite of silver, is then treated on the filter with a somewhat concentrated solution of ammonia, which dissolves the plumbite of silver. The ammonia is expelled from the filtrate by

[1] Berichte der deutschen chemischen Gesellschaft, **15**, 262.
[2] Zeitschrift für analytische Chemie, **21**, 214.
[3] This Journal, **3**, 229; Zeitschrift für analytische Chemie, **20**, 416.
[4] Berichte der deutschen chemischen Gesellschaft, **15**, 307 and 1264.

evaporating on the water-bath and the residue dissolved in nitric acid. The silver is then detected in one of two ways: either by treating with caustic soda solution and thus obtaining the characteristic precipitate of silver plumbite, or by precipitating the lead as sulphate, filtering and treating the filtrate with hydrochloric acid.

Wöhler,[1] in 1837, published a short notice on the fact that caustic soda precipitates a silver and lead compound from solutions of these metals; but since Krutwig's determinations of the composition of this substance do not agree with those of Wöhler, he gives the results of his analyses, which indicate the formula PbO_2Ag_2, and this he calls *silver plumbite*. The silver in this compound may be satisfactorily determined by precipitating with hydrochloric acid and washing with hot water to remove the lead chloride, or by electrolysis in cyanide of potassium solution. When silver is present to the extent of only 0.001 gram the method is not applicable.

Krutwig has also successfully applied Luckow's[2] qualitative method of electrolysis (in ammonia or ammonium carbonate solutions) to the quantitative determination of silver by adding ammonium sulphate to the ammoniacal silver solution.

Nickel and Cobalt.—A. Jorissen[3] recommends, for the separation of small quantities of nickel in the presence of cobalt, treatment of the solution with caustic soda, then with a few drops of bromine water, and finally with a few drops of potassium cyanide solution. The nickel hydroxide is reduced and dissolved, while the cobalt precipitate is not affected even by an excess of the potassium cyanide, but remains suspended in the liquid in the form of black flakes.

If much nickel and little cobalt are present, the latter likewise goes into solution.

Chromium.—Ad. Carnot[4]: "On chromium phosphate and its utilization in analysis and industry."

According to the author, chromium in its chlorides, sulphates or acetates (either green or violet), but not in its oxalates, may be expeditiously and satisfactorily determined as follows: a weakly acid solution of the chromium salt is heated to boiling, and an alkaline phosphate and sodium acetate are added; all the chromium is precipitated as phosphate. The method is equally applicable to chromates; in this case sodium hyposulphite is added as a reducing agent.

The precipitate is washed with a hot solution of sodium acetate, and then with ammonium nitrate. The method is specially valuable in operating in presence of chlorides and sulphates.

[1] Poggendorff's Annalen, **41**, 344.
[2] Zeitschrift für analytische Chemie, **19**, 1.
[3] Zeitschrift für analytische Chemie, **21**, 208.
[4] Bulletin de la Société chimique, **37**, 482.

F. P. Treadwell:[1] "On the determination of chromium." Th. Wilm[2] has observed that determinations of chromium as oxide give too high results when the precipitation with ammonia is effected in *glass vessels;* results obtained by him in potassium bichromate are: (Cr_2O_3) 55.76, 57.89, 53.92, 55.32, 54.92; calculated, 51.82. Treadwell has therefore made determinations both in glass and in platinum, and his results are satisfactory in either case as shown by the following figures: in glass (Cr) 35.48, 35.49, 35.46, 35.47; calculated 35.54. He accounts for Wilm's results by saying that the glass used by the latter may have been of poor quality. Wilm also stated that chromic oxide ready for final weighing contains chromate; Treadwell finds this to be true, but states that the amount is so small that it cannot be weighed.

M. Richter[3]: "On the alkalinity of potassium chromate." Also, "On a new volumetric method for the determination of potassium bichromate and application of the same as a titrating substance for caustic alkalies."

Richter has found that the apparent alkalinity of potassium chromate when tested with litmus is due to the oxidation of the coloring matter, and not to true alkalinity. Phenolphthaleïne is not affected by the chromate; but if a trace of alkali be added, the real alkalinity thus produced is rendered immediately apparent by the change in color of this indicator. On this fact he bases a method for determining bichromates. To determine both chromates and bichromates in any neutral solution, the bichromate is first estimated by means of a standard solution of an alkali with use of phenolphthaleïne as an indicator; the whole chromic acid is then precipitated in a measuring flask by means of a standard solution of silver nitrate, which is added in excess, and its quantity ascertained by estimating the excess of silver in a measured portion of the liquid. The bichromates may be employed for the volumetric determination of the caustic alkalies and ammonia.

B. Reinitzer[4]: "Studies on the conduct of the acetates of chromium, iron and aluminium."

The results of Reinitzer in this investigation are valuable, not only in their bearing on analytical chemistry, but also because they seem to settle in a satisfactory manner certain previously doubtful points relating to the pure, individual substances. The most complete text-books contain insufficient statements in regard to the acetate of chromium, which, owing to the manifold analogies existing between chromium, aluminium and iron, might be expected to conduct itself similarly to the acetates of the two latter metals. If a solution of chromium sulphate or chloride is treated with an excess of sodium acetate solution and boiled, no precipitate separates out, however concentrated the solution or great the

[1] Berichte der deutschen chemischen Gesellschaft, **15**, 1392. [2] *Ibid.* **15**, 2223.
[3] Zeitschrift für analytische Chemie, **21**, 204. [4] Monatshefte für Chemie, **3**, 249.

amount of sodium acetate used may be. When boiled, even for a short time, the solution on cooling assumes a violet color, and the properties of the chromium solution are now found to have been strikingly changed. The caustic alkalies, ammonia, ammonium sulphide, alkaline carbonates, and various other reagents now fail to produce in the cold solution even the slightest turbidity. It was found, further, that this chromium solution imparts to a certain amount of iron or aluminium acetate the same passive condition towards the above reagents; and, as a result of this fact, that the method of separating iron and aluminium from other metals which is based on the precipitation of these metals as basic acetates, becomes inapplicable in both qualitative and quantitative analyses whenever chromium salts are present.

In order to further investigate these phenomena, the acetate of each of the three metals was prepared in pure condition, and its conduct, both alone and in mixtures, examined. The preparation of pure acetate of chromium was attended with difficulties, but was finally effected through the double decomposition of lead acetate and chromium sulphate, the latter having been prepared from purified commercial chromic acid by treatment with sulphur dioxide.

The concentrated solution of lead acetate was added in slight excess to the solution of chromium sulphate, and the mixture allowed to stand for several days to effect a more complete precipitation of the lead sulphate. The excess of lead was then precipitated by sulphuretted hydrogen, the excess of which was afterwards removed by means of a current of carbon dioxide. The solution of chromium acetate thus obtained is violet in color, but yields, on being evaporated to dryness on the water-bath, a green residue, which, when redissolved, produces a green solution. If this green solution is boiled with sodium acetate it becomes purple violet on cooling. Both of these modifications of chromium acetate show in themselves as well as towards reagents the same conduct as the chromium salts of inorganic acids when the latter are boiled with sodium acetate. This fact of the passive condition of chromium acetate explains why, in the quantitative analysis of chromates, the solution, after reduction with sulphuric acid and *alcohol*, must be evaporated to dryness before the chromium can be precipitated by ammonia.

Pure ferric acetate was prepared by precipitating the hydroxide with ammonia in the cold, washing with hot water until no trace of ammonia or chlorine could be detected in the filtrate, and then dissolving in acetic acid. Contrary to all previous statements and contrary to the author's explanation, the clear blood-red solution thus obtained can be evaporated on the boiling water-bath to dryness without furnishing an insoluble residue. If the heating of the dry substance on the water-bath is continued for a time, the metahydroxide can be subsequently precipitated from its solution by means of sodium acetate or hydrochloric acid; if the heating is continued an hour or two the residue becomes insoluble in water.

Very few chemists appear to have obtained perfectly pure ferric acetate; for in all chemical books it is stated as characteristic of ferric acetate, that the iron is precipitated as basic acetate when dilute solutions of it are boiled. This is not true of the pure salt. If, however, an alkaline acetate is added, precipitation is readily effected.

Aluminium acetate was prepared by dissolving the sublimed chloride in water, precipitating from the hot solution with ammonia, dissolving in sulphuric acid and treating with lead acetate, the excess of lead being removed with sulphuretted hydrogen. The solution thus obtained cannot be evaporated on the boiling water bath without giving an insoluble residue. It differs, therefore, in this respect from the acetates of iron and chromium. It is, however, only after a certain concentration has been obtained that a basic acetate separates out. If the water lost by evaporation is continually replaced no precipitate of basic acetate takes place, provided no alkaline acetate is present.

The following statements give the results obtained by mixing the acetates:

If a solution of *green* chromium acetate is treated with a little acetate of iron and the mixture boiled, the iron is deposited as a flocculent precipitate. If the iron acetate is in excess and the green chromium acetate gradually added to it, the solution is maintained up to a certain point when a part of the iron is precipitated.

If however a solution of chromium acetate which was originally *violet*, is treated with acetate of iron, no precipitation takes place, even though the quantity of iron salt added is large and the boiling is long continued.

The amount of iron acetate which becomes passive through the influence of chromium acetate depends upon various conditions; such as the amount of the iron acetate, the concentration of the liquid, whether the two are brought together when cold or hot, etc. Detailed experiments are described showing the effect of these conditions.

The effect of chromium acetate on aluminium acetate is in general the same as on iron acetate, except that aluminium acetate can not be precipitated by *green* chromium acetate.

Tin.—M. M. P. Muir[1]: "Detection of tin in presence of antimony." The mixed sulphides are dissolved in strong hydrochloric acid, and the stannic reduced to stannous chloride by boiling with copper turnings, after which the presence of tin can be detected by adding mercuric chloride.

Uranium.—Clemens Zimmermann[2]: "Investigations on Uranium." In 1846 Margueritte published a description of the now

[1] Chem. News, **45**, 68. [2] Annalen der Chemie, **218**, 285.

well-known volumetric method for the quantitative determination of ferrous salts which depends upon the reduction of potassium permanganate. Until 1861 this method was applied indifferently to solutions containing either sulphuric or hydrochloric acid. Löwenthal and Lenssen at this time showed conclusively that if hydrochloric acid be present in the solution, chlorine is liberated, owing to the oxidizing action of the permanganate, and that errors are thereby introduced. Fresenius verified these conclusions and recommended the use of sulphuric acid when possible, and in other cases the following modification, *i. e.* the ferrous solution is diluted to ½ litre; of this 50 cc. are added to a larger amount of water acidified with H_2SO_4 and the solution titrated with permanganate; then 50 cc. more are added and a second titration effected, also a third and fourth. The results of the third and fourth determinations are found to be correct.

Zimmermann now modifies the Margueritte method by introducing into the ferrous solution *containing hydrochloric acid* manganous sulphate, which prevents the liberation of chlorine, and consequently the errors known to exist when the manganous salt is not used.[1]

The manganous sulphate solution is obtained by dissolving 100 grams of the salt in water and diluting to about 500 cc. 20 cc. of this solution are sufficient even in presence of 50 cc. hydrochloric acid (1.12 sp. gr.) to render the results of the titration of ferrous salts by potassium permanganate absolutely exact. The permanganate is added slowly with constant stirring.

Zimmermann also applies this method to the volumetric determination of uranous salts. If uranic salts in solution be treated with sulphuric acid and zinc they are converted into uranous salts and the reduction goes no further.

For the determination of uranous salts Zimmermann has also proposed the following method: An acid solution of potassium bichromate oxidizes uranous salts just as quickly and perfectly as potassium permanganate; moreover, it liberates iodine from potassium iodide; the liberated iodine can then be converted into sodium iodide by means of sodium hyposulphite. Accordingly, to determine uranium, the reduced salt in solution is acidified with hydrochloric acid, then an excess of a solution of potassium bichromate of known strength is added, and the whole diluted with water to about 150 cc., and with constant stirring a solution of potassium iodide is added. The iodine liberated is determined by means of a standard solution of sodium hyposulphite with use of starch solution. Finally, an iodine solution of known strength is added until the formation of the blue iodine-starch compound is noticed. The results thus obtained agree closely with those obtained by the Margueritte method.

[1] It is now clear that the correct results obtained by Fresenius in the third and fourth repetitions of the titration are due to the accumulation of *manganous* compounds in the solution in which the determination is being made.—H. N. M.

Molybdic Acid.—Otto Freih. v. d. Pfordten:[1] "Volumetric method of determining molybdic acid." Molybdic acid is quickly reduced by zinc and hydrochloric acid. The following method is analogous to Zimmermann's method for uranium (see above).

The salt to be determined is dissolved in a little water and 60 cc. of a 27 per cent. hydrochloric acid are added; 8 to 10 grams of zinc in sticks are then introduced (the amount of iron in which has been previously determined by titration). When the liquid has become yellow in color, and before the zinc is completely dissolved, the vessel is cooled; the liquid is then transferred to a porcelain dish, in which are contained dilute sulphuric acid and manganous sulphate, and titrated with permanganate, with active stirring, until a rose tint appears.

W. C. D.

NOTES.

Filtration Balance.

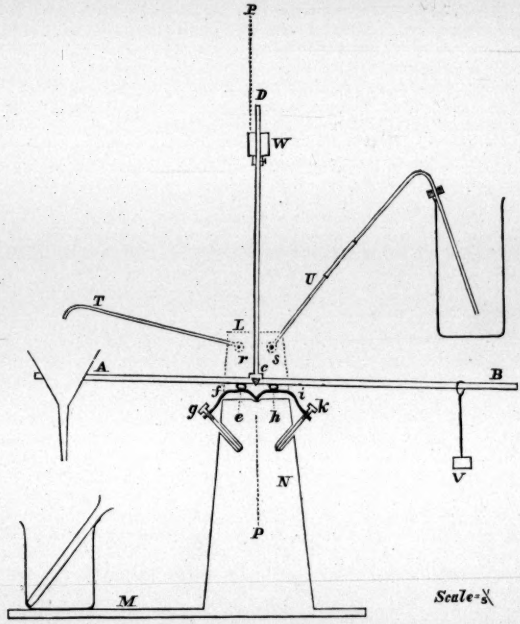
All the arrangements for the automatic washing of precipitates, of which I have seen previous mention, provide for keeping the water at nearly a constant level in the funnel. By this method of washing a precipitate, usually much more water is necessary than if each portion of water is allowed to drain off before a new addition of it. At the Cincinnati meeting of the American Association for the Advancement of Science in 1881, Prof. H. Carmichael, of Bowdoin College, Maine, exhibited a filtration and evaporation balance, which I must describe before giving my modification of it. The figure, without the upright CD, illustrates this balance, which is most convenient for delivering a large amount of liquid on a small filter or into a small evaporating dish.

A beam AB balanced on the knife-edge (or pivot) C, supports in a ring, A, the funnel which is equipoised by the weight V. *s* and *r* are corks passed through the upright NL, and hold in any position the tubes U and T, which are bent to pass through them. Close to C, and under the beam, passes a rubber tube *e*, which connects the tubes U and T and conducts the wash-water or other liquid. By use of thumbscrews *g* and *k* the little brass arms *f* and *i* may be raised to adjust the pressure upon the rubber tubes *e* and *h*.

To the above-described apparatus, I add a vertical rod CD fastened to the arm AB and at right angles to it; on this is supported a weight W, whose height is fixed by the binding screw

[1] Berichte der deutschen chemischen Gesellschaft, 18, 1925.

also sliding on this rod. I employ for two-inch funnels a cylindrical lead weight V, weighing about 300 grams; for three-inch funnels about 500 grams. The apparatus is used as follows:



Having brought all the precipitate on the paper in a funnel, allow it to drain, put the funnel in place and fix the weight W near D, then slide the weight V on B until it will just be able to raise A from its lowest position, when of course W will move to the right of the vertical PP. Then water will pass through *e* and drop into the funnel until it is nearly full, when (if W and *k* are adjusted properly), A will fall, bringing W to the left of the vertical, and in this position no water will pass through *e*. When the funnel has again drained, the arm A rises, and (the water again flows into the funnel) this alternating motion continues so long as water is supplied. I have made AB of iron 10x4 mm. The upright NL is 35 mm. thick; other dimensions may be taken from the figure.

It is essential that the tube *e* admits of being closed by very gentle pressure (less than 100 grams) of the knife-edge cut on the under side of the beam. I use for this pure rubber tubing 2.5 mm. exterior diameter.

Removing W the apparatus may be used as was intended by Prof. Carmichael. When conducting an evaporation, the dish rests in A and the gas passes through *h* to the burner, so that when the liquid is exhausted, and before that in the dish has come to dryness, the arm A will rise, compress *h*, and so extinguish the flame.

F. P. DUNNINGTON.

UNIVERSITY OF VIRGINIA, *January*, 1883.

Helvite from Amelia County, Virginia.[1]

Helvite has been recently found in small quantity by H. C. Lewis at the Mica Mines, near Amelia Court House, Virginia. It occurs in small sulphur-yellow crystals and crystalline masses associated with orthoclase and garnet. An analysis of the carefully picked mineral was made by R. Haines with the following results: Specific gravity 3.29.

SiO_2	32.32
BeO	11.47
Al_2O_3	2.68
MnO	45.38
FeO	1.85
CaO	.64
K_2O	.39
Na_2O	.92
S	4.50
H_2O	.30
	100.45
Less oxygen replaced by sulphur	2.25
	98.20

The glucina was separated by boiling with NH_4Cl (Berzelius's method). For the estimation of SiO_2 two portions of the mineral were taken, one of which was treated in the usual way for the total silica, and the other, while still moist, was treated several times with a boiling concentrated freshly made solution of sodium carbonate, and the washed residue weighed. This residue (in the analysis above given) of 9.22 per cent. was considered to be silicious gangue (insoluble silicate), and the difference from total silica to be the true gelatinous silica of the mineral species. Accuracy of this determination being doubtful, owing to the very small

[1] Abstract furnished by the author.

amount of the mineral at command, a second determination was made on larger quantities (1 gram and ½ gram) also carefully picked from another sample of the mineral received later. In this was found total SiO_2 32.49 per cent., of which 5.19 per cent. was insoluble gangue.—(*Journal of Franklin Institute*, July and October, 1882.)

Water Analysis.[1]

For the ammonia method of water analysis, R. Haines recommends the following working details supplementary to the directions of Wanklyn.

The glass retort should have its neck sufficiently narrow to be thrust easily five or six inches within the tube of the Liebig condenser, and a short piece of wide rubber tubing slipped up the retort neck should connect them.

Before connecting, cleanse retort with strong H_2SO_4, and also, if necessary, with strong HCl, and wash thoroughly every part of the apparatus. After connecting, flush the whole apparatus with clean tap water introduced at tubulum of retort, and remove water from retort by a glass syphon. By removing the permanganate solution with the syphon, and repeating the flushing with water after each analysis, it will not be necessary to disconnect the apparatus for a considerable time in the case of most potable waters. Violent bumping sometimes occurs during distillation, even of pure soft spring waters as well as some very impure waters. Disasters from this cause are best avoided by quickly removing the burner from below the retort until the foam subsides, and by regulating the flame by a screw compressor. Introducing ignited pumice, &c., tapping or shaking the retort or inclining the retort upward, are not to be recommended. The current of water passing through the condenser must be constant and sufficiently rapid. The distillation should invariably be continued until less than .005 mgm. NH_3 is found in 50 cc. of distillate, both of free and albuminoid ammonia. In highly ammoniacal waters the free ammonia is best distilled off in one portion of 200 or 250 cc., which is diluted and an aliquot part nesslerized. Such waters sometimes yield considerably more than three-fourths of their whole free ammonia in the first 50 cc. of distillate. The Nessler cylinders should be made of thin colorless test tube glass, fifteen centimetres in height and twenty-three millimetres in internal diameter, with thin slightly depressed bottoms so as to stand firmly. Moulded cylinders are not satisfactory. Addition of not more than .5 cc. of Wanklyn's NH_4Cl solution, *after* the addition of Nessler solution, generally does not produce turbidity, so that an already nesslerized cylinder of deficient color may be strengthened to that extent. The colors are generally best observed by placing the cylinders on a white tile

[1]Abstract furnished by the author.

and looking perpendicularly downward, then raising them slightly and placing a second tile below at an angle of 45°, and also with deep colors by holding the two cylinders side by side against a white tile held vertically and opposite to the light. These observations, rapidly made, serve to check each other, which is especially advantageous if the liquids have become slightly turbid. But it is generally best not to attempt to estimate accurately colors deeper than that produced by about .06 mgm. NH_3 in 50 cc. water. The operator should also take the precaution to ascertain that he is free from color-blindness.

In regard to cleanliness of apparatus, directions cannot be made too emphatic. Thorough and frequent washing with ordinary good water, all apparatus, as well as the lips of the reagent bottles, immediately before actual use is most essential, and must be scrupulously performed. No other work involving the use of ammonia or its volatile compounds should be permitted in the same room during the water analysis.

As regards the reagents it is of very great importance to have the alkaline permanganate solution perfectly free from ammonia. It should be prepared with good common distilled water, and boiled actively for four or five hours, and finally made up to one litre with distilled water which has been perfectly purified from ammonia and organic matter by careful distillation with pure alkaline permanganate solution. Ordinary white stick potash may be used in commercial condition. Dissolve 200 grams KHO and 8 grams $KMnO_4$ in separate portions of water of more than one-half litre each, and pour slowly, with stirring, the former solution into the latter, but not *vice versa*. The boiling solution should not concentrate at any time much below one-half litre, otherwise loss of oxygen ensues with conversion into manganate.

It is quite unsafe to use an impure solution of permanganate and make a correction for that ammoniacal impurity.

If the Nessler solution has been made sufficiently sensitive, the *full* color with ammonia will be developed almost immediately, although amounts of from .005 to .010 mgm. NH_3 require more time than larger quantities, but not exceeding two minutes in the former case. The whole set of nesslerizings can therefore generally be completed within a very few minutes, without mechanical aids of any kind.

Peculiar odors are occasionally noticed in the distillates of free ammonia, which are probably due to unestimated volatile organic matter. To provide for such substances, if nitrogenous, it is advisable to repeat the distillation with permanganate alone on a fresh portion of the sample, preserving the ratio of one to six between the permanganate solution and the water. Prof. Remsen and Mr. Marsh, of Princeton,[1] have observed striking differences between the added free and albuminoid ammonia and the total ammonia obtained as

[1] This Journal, **4**, 3, 138.

above indicated. Haines has also analyzed a well water of which the free ammonia distillate had a strong odor of organic substance, resembling that which the water itself had when warmed, but more intense. The water contained a large amount of vegetable matter of fungoid character. Free and albuminoid ammonia were both in very large excess, but chlorine, nitrates and total solids in amounts not greater than in pure soft spring water.—(*Jour. Franklin Institute*, Nov. 1882, 342.)

On Benzenes of Different Origin.

Experiments by VICTOR MEYER show that there are some differences between benzene obtained by fractional distillation from coal-tar and carefully purified, and that obtained from benzoic acid. A short time ago Baeyer showed that benzene unites with isatin to form indophenin:

$$\underset{\text{Isatin.}}{C_8H_5NO_2} + 2C_6H_6 = H_2O + \underset{\text{Indophenin.}}{C_{20}H_{13}NO}.$$

Meyer now shows that, while this is true of the purest benzene obtained from coal-tar, it is not true of that obtained from benzoic acid, whether the benzoic acid be extracted from urine or made from resin or toluene. He shows, further, that if coal-tar benzene is treated for about ten hours with concentrated sulphuric acid on a water-bath, then washed and redistilled, it loses the power of uniting with isatin. If the benzene-sulphonic acid which is formed in the process of purification is purified and reconverted into benzene by dry distillation, the benzene which is thus obtained has the power of uniting with isatin. The purest commercial benzene loses the power of uniting with isatin if shaken for ten minutes with concentrated sulphuric acid, and also if shaken for a short time with isatin and sulphuric acid. By way of explanation of the phenomena described, three hypotheses are mainly to be considered:

1. It is possible that, in the purest benzene obtainable from coal-tar, there is a minute quantity of some foreign substance which cannot be detected by any ordinary means, and which may, something like zinc dust or aluminum chloride, exert a kind of catalytic action, rendering the ordinarily indifferent benzene susceptible to the influence of isatin.

2. The contrary supposition may also be true, viz. that the benzene from benzoic acid contains a minute quantity of some impurity.

3. Benzene from coal-tar may contain two bodies, physically and chemically very similar, which nevertheless differ in their chemical activity—the more active one combining with isatin, and being first transformed by sulphuric acid into its sulphonic acid. The less active one would then be the chief constituent of the benzene from benzoic acid.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2893.)

Nascent Hydrogen.

D. TOMMASI has for some time past been engaged in trying to determine whether the reducing properties of hydrogen, in what is called the nascent state, are due to an allotropic condition or to new thermal conditions. He has studied a large number of reductions effected by hydrogen which are usually attributed to its nascent state, such as:

Reduction of silver chloride, bromide or iodide;
" of chloric acid and the chlorates;
" of ferric chloride;
" of nitrates;
" of chloral.

The results obtained may be stated in brief, as follows:

Silver chloride, in suspension in water acidulated with sulphuric acid, was treated with sodium amalgam. The experiment was performed in the dark and lasted forty minutes. No reduction took place. Similar experiments with the same result were performed with the iodide and bromide. On the other hand, an electric current can decompose the chloride in suspension in acidulated water. The author asks how the fact can be explained that silver chloride, which resists the action of nascent hydrogen formed by the decomposition of water by sodium amalgam, can be reduced by hydrogen, also nascent, which is formed by the decomposition of water by the electric current?

A saturated solution of potassium chlorate was acidulated with sulphuric acid and then divided into two parts. One part was treated with zinc, the other with sodium amalgam. In the former there was an abundant formation of chloride, while in the latter there was no change.

A solution of potassium perchlorate was treated with, 1. zinc and sulphuric acid; 2. magnesium and dilute sulphuric acid; 3. copper sulphate and zinc; 4. sodium amalgam; and 5. zinc and potassium hydroxide, but reduction could not be effected. When treated, however, with sodium hydrosulphite, a compound which does not give off hydrogen, the perchlorate is easily transformed into the chloride: $4SO_3HNa + KClO_4 = KCl + 4SO_3NaH$. Further, this reduction is also effected by hydrogen evolved by the action of zinc on sodium bisulphite, $HNaSO_3$.

It cannot be explained why nascent hydrogen, which is formed by the decomposition of water at ordinary temperature by zinc dust, transforms potassium nitrate into nitrite, ferricyanide into ferrocyanide, reduces indigo and the iodates, but does not reduce chlorates.

Now, if nascent hydrogen is always the same thing, if its properties are inherent, it should always effect the same chemical changes, but the experiments described show clearly that the reducing power of nascent hydrogen varies according to the chemical reaction which produces it. And if the gas, in the nascent state, is en-

dowed with stronger affinity than in the ordinary state, this is due solely to the fact that the hydrogen at the moment it passes out of a compound is accompanied by all the heat which is produced when it is set free. Hence nascent hydrogen is synonymous with hydrogen + calories.[1] Indeed, all the reductions which can be effected by nascent hydrogen can be equally well effected by ordinary hydrogen at an elevated temperature. And the reason why hydrogen, produced by different chemical reactions, has different reducing powers, is that these reactions do not develop the same quantities of heat.—(*Bulletin de la Société chimique*, **38**, 148.)

Atomic Weight of Yttrium.

The atomic weight of yttrium has been redetermined by Cleve, upon pure material which was proved to be free from terbia. As a mean of twelve experiments upon the synthesis of yttrium sulphate, he found the percentage of yttria in the latter to be 48.503, ± .0029. Hence Yt = 88.9, ± .027; or, if $SO_3 = 80$, then Yt = 89.02. The calculations are Cleve's, including the probable errors. The last figure suggests a pretty close conformity with Prout's law.

F. W. C.

Proposed Monument to Wöhler.

A circular has been sent out by the German Chemical Society, in which contributions are requested for the purpose of erecting a monument to Friedrich Wöhler. There are special reasons why American chemists should be well represented in the list of contributors. A sub-committee will soon be formed to facilitate the collection of money in this country, and it is hoped that especially the many among us who have profited by Wöhler's instruction and to whom the memory of the Göttingen laboratory will always remain among the brightest, will promptly respond. The sub-committee will issue a circular in the course of a few weeks.

[1] If we represent nascent hydrogen by the formula H + a (a designating the calories disengaged by the chemical reaction which produces the hydrogen), we have for a the following values:

$SO_4H_2 + Zn + Aq$;	a = 38 cal.
$SO_4H_2 + Cd + Aq$;	a = 23.8 cal.
$SO_4H_2 + Mg + Aq$;	a = 112 cal.
$2ClH + Zn + Aq$;	a = 34.2 cal.
$2BrH + Zn + Aq$;	a = 34.2 cal.
etc.	etc.

As we see, the value of a varies for each chemical reaction, and consequently the hydrogen will be the more active the greater the value of a. For sodium amalgam a would be equal to about 112 cal.